Preparation of Copolymers of Acrylic Acid and Acrylamide for Copper (II) Capture from Aqueous Solutions

by

Yudong Zhang

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Chemical Engineering

Waterloo, Ontario, Canada, 2009

AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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ABSTRACT

Cross-linked copolymers of acrylic acid (sodium acrylate) and acrylamide were synthesized by free radical polymerization. The copolymer hydrogel was studied for capture of copper ion from aqueous solution. Effects of macromolecular structure (i.e., content of the acrylic acid, the quantity of the carboxyl groups neutralized with sodium hydroxide, and the degree of cross-linking) on water-sorption and copper ion uptake were investigated. With an increase in the content of acrylic acid (sodium acrylate), the copper sulfate uptake increases, and water sorption decreases quickly and then slowly increases when the acrylic acid content is high enough. The copper ion uptake is accompanied with a release of sodium ions from the copolymer. Increasing the percentage of the carboxyl groups neutralized by sodium hydroxide will increase the uptake of copper sulfate and water. With an increase in the content of the cross-linking agent, both copper sulfate uptake and water sorption decrease. Even though valence of copper ion is two times that of sodium ion, the copper ions sorption and sodium ions release do not follow a simple ion exchange relation because of insertion of acrylamide co-monomers in macromolecular chain. When copper ions interact with carboxyl groups in the copolymer to form chelating complexes, the water sorption decreases substantially.

An analysis of adsorption isotherm indicates that at relatively low concentrations of $CuSO_4$ in water, the copper ion sorption into the copolymer follows the Langmuir model. The wide angle X-ray diffraction (WAXD) data reveal that the copper sulfate sorbed in the hydrogel is not in crystalline state.

ACKNOWLEDGEMENTS

I am grateful to reach another milestone in my life! I would like to take this opportunity to thank my supervisor, Professor Xianshe Feng, for his invaluable guidance, encouragement, constructive criticism and support in the period of this study and preparation of the thesis.

I gratefully express deep appreciation to Dr. Gil Francisco for his help in preparation of thesis and Dr. Hui Li for his invaluable advice and discussion in theoretical analysis. I also would like to thank the people in the membrane laboratory for their assistances.

More importantly, I would like to deeply acknowledge my wife and daughter for their endless support throughout my study. Without their support, I could not be able to complete this study. In addition, it is also impossible for me to keep working on this degree without the assistance from my relatives in PR China for their financial support.

Finally, I would like to acknowledge: Ontario Graduate Scholarships in Science and Technology (OGSST), Ontario Student Assistance Program (OSAP) and the bursary from the University of Waterloo.

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CHAPER 1 INTRODUCTION

1.1 Background

Hydrogels are a group of (co)polymers with cross-linked networks. Their structures are heterogeneous in different orders in micro-morphology [Osada 1998]. Many methods are available to prepare hydrogel materials. They are mainly made from water-soluble monomers by radical polymerization reactions. The most popular water-soluble monomers include acrylic acid, acrylamide and their derivatives. These monomers can be used to synthesize cross-linked homopolymers and copolymers consisting of different co-monomers by aqueous solution or other polymerization processes. These monomers also can be grafted onto such other materials as polyethylene terephthalate (PET) fiber and some natural macromolecules to obtain hydrogel materials. Another way to synthesize hydrogel materials is to prepare interpenetrating polymer network (IPN) composites from water-soluble monomers with other materials. In addition, some natural materials (e.g., chitosan) are also used as hydrogels.

The wet and soft hydrogel materials are based on cross-linked hydrophilic polymers. Some hydrogel materials are cross-linked polyelectrolytes with ionic groups on the macromolecular chains. Therefore, the polyelectrolyte gels possess unique physical and chemical properties [Tanaka 1982, Ilmain 1991, Okuzaki 1995, Woessener 1970, Osada 1992]. They can hold a large amount of water molecules (over 2000 times the polymer weight) in their pores of the network but do not dissolve in aqueous solutions [Osada 1992]. Because of the ionic groups on the macromolecular chains, polyelectrolyte has an electrostatic potential field around the macromolecular chains [Osaka 1998]. Therefore,

they can also attract certain cations or anions to form complexes. One of the most important applications of hydrogel materials is to bind and capture metal ions (especially heavy metal ions) from water. Isogai [1999] found that polyelectrolyte binds metal ions in three ways: 1) Cooperative and stoichiometric. 2) Non-cooperative and stoichiometric, and 3) Cooperative and non-stoichiometric. The mechanism of metal ion adsorption is determined by the three-dimensional chemical structure of the ligand, hydrophobicity and the charge density of the polyelectrolyte [Osada 1998].

Heavy metal ions are harmful and toxic to human beings and the environment [European Commission 2002, Lester 1987, Zhao 2004]. For example, copper ions can damage kidneys and the liver, causing anemia. In this thesis work, hydrogels based on acrylic acid (sodium acrylate) and acrylamide copolymers were studied for water sorption and copper (II) ion removal from aqueous solution.

The effects of the content of the acrylic acid in the copolymers, the quantity of the carboxyl groups neutralized by sodium hydroxide and the content of the cross-linking agent on the sorption performance were evaluated. The adsorption equilibrium of the copper ions in the copolymer hydrogels was investigated at different copper ion concentrations. It was observed that copper ion uptake was accompanied with replacement of sodium ions, and water molecules were forced to leave the copolymer hydrogels. The crystalline morphology of copper compounds was examined by wide angle X-ray diffraction (WAXD) to confirm that they are not crystalline in the hydrogel materials.

1.2 Scope of the thesis

This thesis includes the following: synthesis of copolymers of acrylic acid (sodium acrylate) and acrylamide, their sorption behavior for copper ion removal from water, and water sorption capacity. In particular, the effect of macromolecular structure on the sorption behavior was studied.

Chapter 1 gives an introduction to preparation of polymer hydrogel materials and their sorption behavior for metal ions and water. The objective of the research is also present in this chapter.

A review of the literature on the subject is presented in Chapter 2, which covers preparation of polymeric hydrogels, adsorption mechanism, and various models currently available for analyzing the experimental data of sorption equilibrium.

Chapter 3 describes the experimental work and Chapter 4 presents the research results and discussion. Specifically, the following are addressed:

A. Synthesis of copolymer hydrogel materials.
B. Investigation on the effect of macromolecular chain structure (including the content of acrylic acid in the copolymers, the quantity of carboxyl groups neutralized by sodium hydroxide, cross-liking agent content) on copper ion uptake and water-sorption capacity.
C. Analysis of experimental data on isothermal sorption and modeling of the adsorption isotherm.
D. Qualitative observation on copper sulfate adsorption.
E. Wide angle X-ray diffraction (WAXD) analysis characterizes the crystalline morphological structure of copper compounds in the hydrogel.

In Chapter 5, the general conclusions drawn from this study are presented and recommendations for further studies are given. All the experimental data are presented in the Appendix.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

Heavy metal ions are harmful and toxic to human beings and the environment. Therefore, they must be removed from wastewater and drinking water. Many techniques have been employed to remove heavy metal ions, including adsorption, chemical precipitation, electro-dialysis, ion exchange and membrane separation [Humphrey 1997, Zhao 2004]. Table 2-1 summarizes the general separation processes and their application for heavy metal removal [Humphrey 1997].

Adsorption is a well known technique widely employed for separation and purification. In removing heavy metal ions from aqueous solutions, adsorbents can bind and capture heavy metal ions from the aqueous solutions. The key part of an adsorption process is the adsorbents. Thus, good adsorbents should be abundant and easy to process, and have high selectivity, large surface area and long service time [Zhao 2004].

So far, many natural materials and synthetic compounds have been used as adsorbents, including bark, lignin, dead biomass, zeolite, peat, xanthate, clay, modified wool and cotton, fly ash, chitosan [Bailey 1999], as well as homopolymer, copolymer and composites of water soluble monomers (e.g., acrylic acid and acrylamide). In the next section, the synthesis and applications of synthetic adsorbent for the removal of heavy metal ions will be discussed. Among the above-mentioned absorbents, chitosan has a good adsorption capacity for heavy metal ions. Chitin is a biomaterial abundant in nature. It can be deacetylated to obtain chitosan. Chitosan adsorption capacity for Cu^{2+}, Cd^{2+},

Cr^{3+}, Hg^{2+}, Pb^{2+} is 222, 558, 92, 1123, and 796 mg per gram adsorbent, respectively [Bailey 1999, Masri 1974, McKay 1989].

Table 2- 1 Separation techniques for removal of heavy metal ions from aqueous solution [Humphrey 1997]

Separation technique	**Advantage**	**Disadvantage**
Adsorption	Economical and efficient for dilute solution	Regeneration needed
Chemical precipitation	Remove most heavy metal ions	Need to adjust pH and break down the complex
Electrodialysis	Remove most ions with electric charge	Unsatisfactory for removal of chelated ions
Ion exchange	Easy removal of heavy metal ions	Fouling and regeneration
Membrane separation	Excellent heavy metal removal	Membrane fouling cost

In principle, the adsorption behavior can be quantitatively described by mathematical models based on adsorption equilibrium and kinetics. These models can be used to predict the adsorption capacity or adsorption rate. For sorption isotherms, there are several models employed for data analysis, and the Langmuir isotherm and Freundlich isotherm are most widely used.

The Langmuir adsorption isotherm equation, developed in 1916, describes the relationship between the molecular adsorption or coverage on an adsorbent surface to the concentration (or gas pressure) of a medium around the adsorbent surface. The basic underlying assumption is that the adsorption rate is equal to the desorption rate, i.e. a dynamic equilibrium is created between adsorption and desorption. Additional assumptions for the Langmuir model also include: ① the adsorbent surface is homogenous; ② adsorption on adsorbent surface is localized; ③ each adsorption site can accommodate only one adsorbate molecule or atom [Do 1998]. This model is well suitable for monolayer adsorption and the Langmuir constant (K_L) shows the strength of adsorbate molecules bound and captured onto the adsorption site. The greater the Langmuir constant, the stronger the molecule adsorption.

$$q_e = \frac{K_L q_{\max} C_e}{1 + K_L C_e} \tag{2-1}$$

where q_e is the equilibrium uptake on adsorbent (mg/g), C_e is the adsorbate equilibrium concentration in solution (mg/L), q_{max} is the maximum equilibrium sorption capacity on sorbent (mg/g), and K_L is Langmuir adsorption constant (l/mg).

The Freundlich adsorption isotherm model is a modified Langmuir model because the simple Langmuir model can not adequately explain certain adsorption phenomenon. It shows the relationship between the concentration of an adsorbate on the surface of an adsorbent and the equilibrium concentration (or equilibrium pressure) of the adsorbates in

solution (gas) at a given temperature. This model can work well for multi-site adsorption and heterogeneous surfaces.

$$q_e = K_F C_e^{\frac{1}{n}} \tag{2-2}$$

where K_F is the Freundlich constant [(mg/g)(L/mg)^n], and n is a dimensionless Freundlich constant. Both of them are a function of temperature.

With respect to an adsorption process, the adsorption rate (kinetics) is another important parameter. Mathematical models have been developed to predict the adsorption rate. The common kinetic models of adsorption include pseudo-first order equation and pseudo-second order equation. The Pseudo-first order equation was proposed by Lagergren in 1898. It is generally expressed in the following form [Sag 2002]:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{2-3}$$

where k_1 (1/min) is the pseudo-first order rate constant, q_e is the equilibrium adsorption capacity, q_t (mg/g) is the adsorption capacity at time t.

Ho (1996) employed the pseudo-second order reaction rate equation to investigate the kinetics of heavy metal sorption onto peat. This equation can be written in the following form:

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \tag{2-4}$$

where k_2 is the rate constant of the pseudo-second order equation (g/mg-min).

2.2 Synthesis and applications of hydrogels of polymers and composites

Hydrogel materials are made from water soluble monomers and have been used in many fields [Ilmain 1991, Osada 1998, Kawaguchi 2000, Nguyen 2002]. Some portions of hydrogel materials are normally based on a functional polyelectrolyte which can easily swell in aqueous solutions but does not dissolve. Due to its hydrophilic property, it can hold a large number of water molecules in its network pores and binds metal ions by its functional polar groups (e.g., carboxylic, hydroxide, sulfuric, amide and amine) distributed on the macromolecular chains. The soft and water-wet hydrogel materials have attracted strong academic and industrial interests. The preparation of hydrogels based on homo-polymers, copolymers and composites as well as their applications for the removal of heavy metal ions will be reviewed. Finally, the adsorption mechanism will be briefly discussed in section (2.3).

2.2.1 Synthesis and application of homo-polymers of water soluble monomer

Water soluble monomers include acrylic acid, acrylamide and their derivatives. Among them, acrylic acid is a popular water-soluble monomer with a significant solubility. This monomer can be easily polymerized, and its pH can be adjusted by an inorganic base. If the resulting polymer is linear, it can easily dissolve into an aqueous solution. However, if it is cross-linked by a cross-linking agent or grafted onto a non-water-soluble material, it will adsorb water molecules and becomes swollen, but will not dissolve in water.

There are many methods for polymerization of acrylic acid. In general, acrylic acid is initiated and polymerized in aqueous solutions using water-soluble initiators (such as $K_2S_2O_8$) (Huang 2007) or oil-soluble initiators (such as 2,2'-azoisobutyronitrile (AIBN) (Rivas and Quilodran 2005). If the polymer obtained is a linear polymer, it can generally dissolve in aqueous solutions with high solubility to form a transparent solution. If a cross-linking agent, for example, *N*, *N'*-Methylene-bis-acrylamide (MBA) is used in the polymerization system, a cross-linked polymer of acrylic acid can be obtained. This non-linear cross-linked polymer cannot dissolve in an aqueous solution, but can hold a large amount of water molecules to form a hydrogel. Figure 2-1 shows the schematic diagram of acrylic acid polymerization.

2.2.2 Copolymers of water soluble monomer (acrylic acid and acrylamide)

Acrylic acid is an organic unsaturated acid. This monomer and its polymers, poly(acrylic acid), usually need to be neutralized by an inorganic base such as sodium hydroxide to adjust its pH for certain applications. Acrylamide is also a common water

soluble monomer. It is a non-ionic compound, appearing a pH of neutralization in aqueous solution. In order to expand the applicability of polyelectrolyte materials, acrylic acid (sodium acrylate) and its derivatives are usually used to produce copolymers with other water-soluble monomers, such as acrylamide and its derivatives. From a molecular structure and molecular design point of view, acrylamide monomer can be inserted into the chain segment of poly(acrylic acid), decreasing the sequence length and tacticity of the acrylic acid chain segment. This is expected to enhance the efficiency of carboxyl groups in poly(acrylic acid) to associate with metal ions. It is important that the co-monomer can improve macromolecular chain structure of poly(acrylic acid) and obtain a desired morphology of the condense state.

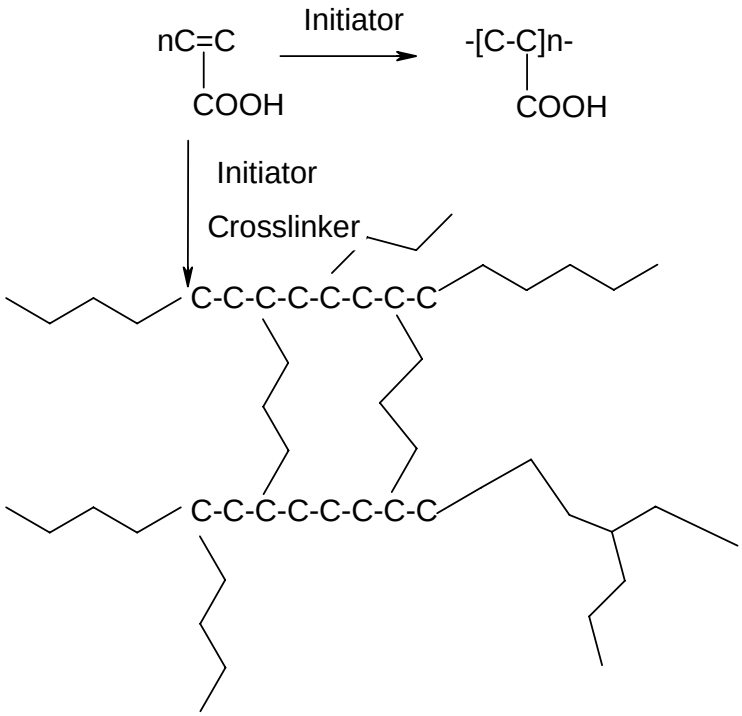

Figure 2- 1 Polymerization of acrylic acid with or without a cross-linking agent

With respect to copolymers of acrylic acid and acrylamide, one important consideration is H-bond formation between carboxyl groups and amides because carboxyl groups on acrylic acid can not only bind metal ions but also act with the amides on acrylamide. Figure 2-2 shows the H-bond complex formation and molecular configuration of the copolymer of acrylic acid and acrylamide [Ilmain 1991]. The H-bond is formed at low temperatures. However, with an increase in temperature, it can dissociate (Figure 2-3). This phenomenon is referred to as the "zipper effect" by Endo [2001]. Formation of H-bond increases the physical cross-linking points of the copolymer, thickening the solution of copolymers, resulting in phase separation and phase transition of the copolymer of acrylic acid and acrylamide.

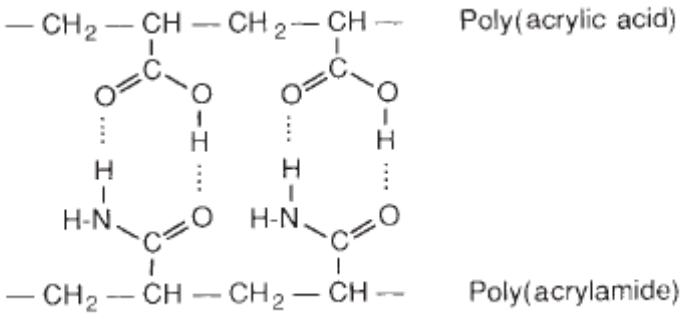

Figure 2- 2 H-bond complex formation and molecular configuration of copolymer of acrylic acid and acrylamide [Ilmain 1991, Katono 1991]

The cross-linked copolymers of acrylic acid and acrylamide are usually used as hydrogel materials to capture metal ions from aqueous solutions [Rivas 1998A, Atta 2008, Cavus 2009]. Cavus [2009] prepared cross-linked homo-polymers of acrylic acid

and copolymer of acrylic acid and methacrylamide (20 mol %). N,N'-methylenebisacrylamide (MBA) was employed as the cross-linking agent (1.0 mol % based on total amount of the monomers). Ammonium peroxodisulphate (APS, 4.5g/100 water) and N,N,N',N'-tetramethylethylenediamine (TEMED) were used as the initiator (1.0 mol % based on total amount of the monomers) and accelerator, respectively. The total initial monomer concentration was 1M. The polymerization reaction was performed at 60 ^{o}C for 24 hours (Figure 2-4).

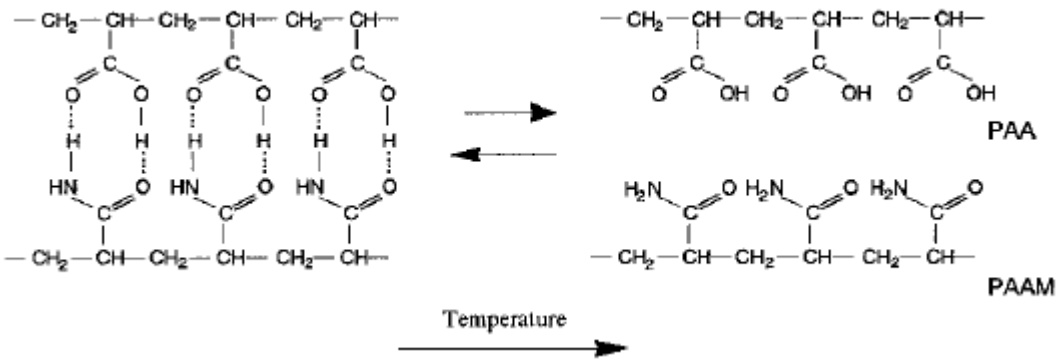

Figure 2- 3 Dissociation of H-bond of the copolymer of acrylic acid and acrylamide with temperature [Endo 2001]

They examined the adsorption behavior of these hydrogel materials for sorption of the heavy metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}), and reported that the homo-polymer had a higher sorption capacity to Pb^{2+}, Cu^{2+} than the copolymers. However, for Cd^{2+} sorption, the difference in the sorption capacity was not significant. It was noticed that as sorption proceeds with time, the pH of the aqueous solution declined, suggesting that the metal ions was bound by the hydrogel materials and the H^{+} was continuously released. The

experimental data show the kinetics of the sorption can be accurately described by the pseudo-second order kinetic model. These (co)polymers can be well used in wastewater treatment industry.

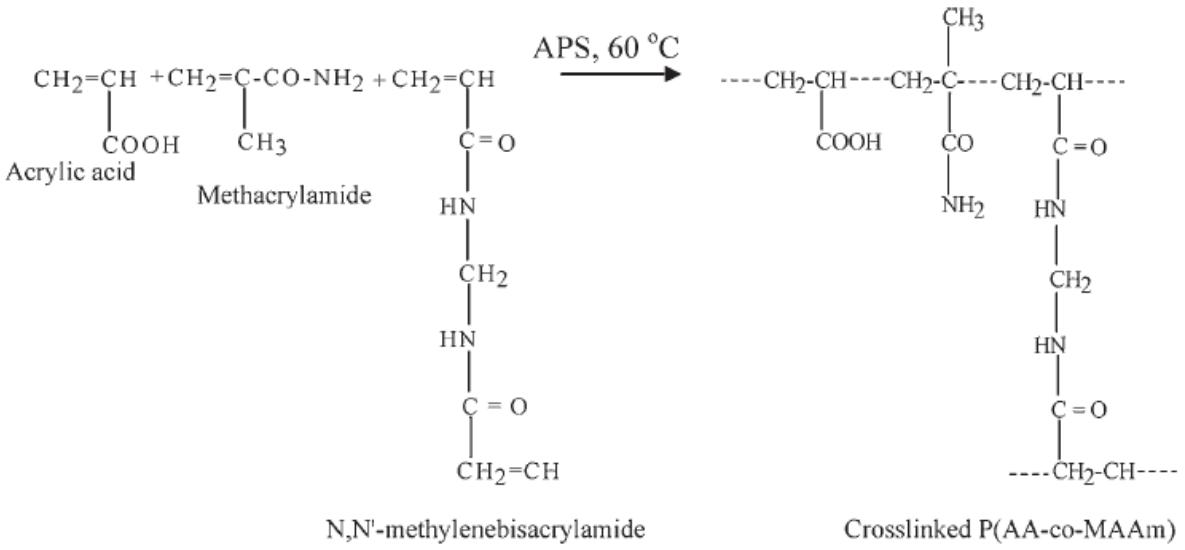

Figure 2- 4 Synthesis of the cross-linked copolymer of acrylic acid and methacrylamide [Cavus 2009]

Xie [2007] prepared a similar hydrogel system to study their adsorption behavior for metal ions (Cu^{2+}, Fe^{3+}). The molar percentage of co-monomer acrylamide used in the polymerization system was about 15 mol %, and 60 % of acrylic acid was neutralized by sodium hydroxide. With increases in adsorption time and the pH from 1 to 4.5, the adsorption amounts (mg/g polymer) of copper ion and iron ion increase. The pH has stronger influence on Fe^{3+} sorption than Cu^{2+} sorption and the copper ions have higher sorption rate than iron ions. With an increase in the initial concentration of the metal ions, the adsorption amount of Cu^{2+} increased continually, but that of Fe^{3+} increased initially

and then decreased when the iron ion concentration was greater than 0.006 M. The hydrogel adsorbent possesses the largest uptake for copper ions and iron ions for 247 and 173 mg/g, respectively. Langmuir model can well describe the adsorption isotherm and the pseudo-second order chemisorption kinetics model can be used to explain the kinetics of adsorption.

The controlled hydrolysis of polyacrylamide in alkaline solution is another important method to prepare copolymers of acrylic acid and acrylamide described by Li [2002]. In their study, the stock solutions of acrylamide (18.75ml, 40 %) and cross-linking agent (7.50ml, 2 %) were mixed with deionized water (23.75ml). The initiator (ammonium persulphate, 70 μl, 10 wt %) and accelerator (*N*,*N*,*N'*,*N*-tetramethylethylenediamine (TEMED), 25 μl, 99 %) were then added to 10 ml of the stock solution. Polymerization was performed at 40 ^{o}C for 1 hour in a glass mold. The obtained samples (in thin sheets) were immersed in deionized water to remove unreacted monomers and linear polymers, followed by partial hydrolysis in 40 ml of 10 wt % sodium hydroxide solution at 75-80 ^{o}C for 5 h. The resulting product was a cross-linked copolymer of acrylic acid and acrylamide. Element microanalysis showed the average sequence structure of the resulting product was 1.8:1 (acrylic acid to acrylamide), i.e., about 64.3 mol % acrylic acid. They studied the adsorption behavior of the hydrogel material for metal ions (Cd^{2+}, Cu^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}). At pH 5-9, the binding capacity (μmol / cm^2-sample) of the copolymer hydrogel was relatively high. Outside this range, the binding capacity becomes very low. With an increase in pH from 2 to 6, the uptake for copper ions and cadmium ions increases from o to 1.59 μmol/cm^2 and 1.56 μmol/cm^2, respectively, and the water sorption capacity increased from less than 10 to120 g/g.

Acrylamide is also a water-soluble monomer. However, it has relatively low capacity (2.7×10^{-2} mmol/g) for metal binding due to the absence of ionic groups. In order to enhance its capacity for binding metal ions, the amides on polyacrylamide chains can be transformed to ionic groups by such chemical reactions as transamidation, Hoffmann and Mannich reactions [Kasgoz 2001 and 2003]. The cross-linked polyacrylamide was prepared by radical polymerization of acrylamide (AAm) plus cross-linking agent (MBA). $K_2S_2O_8$ and $KHSO_3$ were used as an initiator couple. The cross-linked polyacrylamide obtained was then immersed in pure water to get fully swollen at room temperature. The transamidation reaction of amide groups in the polyacrylamide chain was performed in aqueous media or non-aqueous media at 90 ^oC for 9 hours by adding ethylenediamine (EDA), diethylenetriamine (DEDA) and triethylenetriamine (TETA) in the reaction system. The products obtained were washed with water and methanol, and dried under vacuum to constant weight. The resulting polymers obtained from aqueous media and non-aqueous media had the maximum capacity of binding copper ion, 2.27 mmol/g-sample and 2.93 mmol/g-sample, respectively. The metal removal capacity of the products obtained from transamidation reaction increases with an increase in pH from 3 to 5.5.

One derivative of amide with ionic groups can also be obtained if the cross-linked polyacrylamide was treated according to Hoffmann reaction. NaOCl can be used to react with the amide groups in the cross-linked polyacrylamide, as shown in Figure 2-5. The cross-linked polyacrylamide was transformed to its cationic derivative. The maximum capacity of the polymer for binding copper ion was shown to be 1.86 mmol/g.

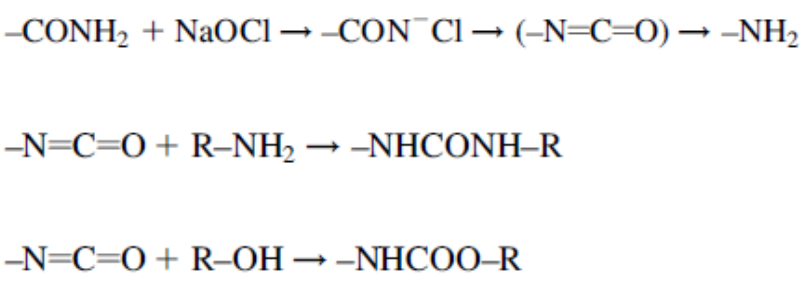

Figure 2- 5 Hoffmann reaction mechanism of cross-linked polyacrylamide [Kasgoz 2001]

Furthermore, Kasgoz [2003] reported that when the amide groups in cross-linked polyacrylamide were treated using HCHO and EDA according to Mannich type reaction, the maximum capacity for the resulting hydrogel product to bind copper ions increased to 2.76 mmol/g from 2.7×10^{-2} mmol/g. Figure 2-6 shows the Mannich reaction mechanism.

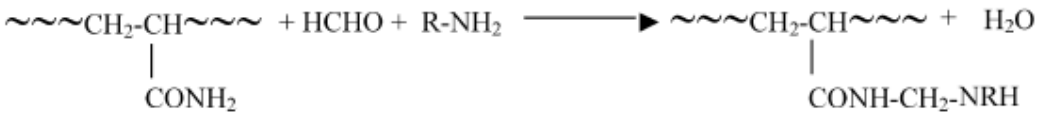

Figure 2- 6 Mannich reaction mechanism of cross-linked polyacrylamide [Kasgoz 2003]

In addition, if the cross-linked polyacrylamide was treated with formaldehyde and sodium bisulfate (sodium sulfate) based on sulfonethylation reaction, anionic derivatives of carboxyl groups can be obtained. Figure 2-7 shows the sulfonethylation reaction mechanism. The resulting hydrogel product has a higher capacity to bind copper ions (4.07 mmol/g).

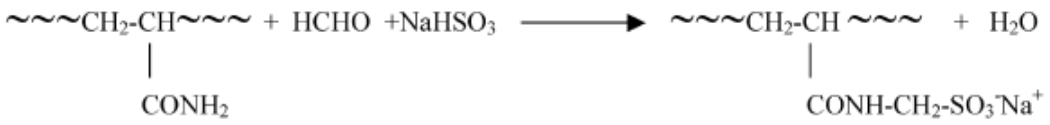

Figure 2- 7 Sulfonethylation reaction mechanism of cross-linked polyacrylamide [Kasgoz 2003]

It is worth noting that with an increase in pH from 3 to 5.5, the binding capacity of the hydrogels treated with both Mannich and sulfonethylation reactions increased. The metal adsorption rate in the hydrogels obtained by the Mannich reaction also increased with an increase in pH from 3 to 4.5.

In addition, the two products obtained also have high removal capacity for Cd^{2+} and Pb^{2+}.

2.2.3 Composites from water-soluble monomers and polymers

Preparation of blends and composites is an efficient and economic method to expand the applicability of water-soluble polymeric materials. Both acrylic acid and acrylamide are widely used in the form of blends and composites.

Polyvinylpyrrolidone (PVP) is a water-soluble polymer, and its macromolecular structure is shown in Figure 2-8. The monomer has a 5-membered lactam structure. Because of the presence of carbonyl groups in the structure, PVP can be dissolved in water and other polar solvent such as ethyl acetate, chloroform, benzene and lower alcohols or ketones.

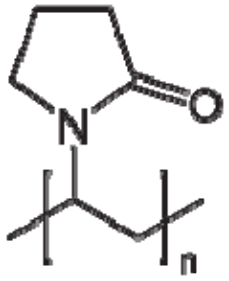

Figure 2- 8 Chemical structure of polyvinylpyrrolidone [Ali 2003]

PVP was used to prepare hydrogel materials by radiation-induced homo/copolymerization with acrylic acid (AAc) [Ali 2003]. Using PVP (MW = 1, 300, 000) and AAc to synthesize hydrogel materials by radiation with $^{60}C_o$ gamma rays initiation at a dose rate 10.28 kGy/h, the resulting polymer had an interpenetrating network (IPN) structure. With an increase in the content of the PVP, the water sorption uptake of the copolymer increased. In addition, this composite was studied about its sorption behavior for metal ions (Fe^{3+}, Mn^{2+}, Cu^{2+}). pH has higher effect on Fe^{3+} than Mn^{2+} and Cu^{2+}. The sorption rate can be described by pseudo-first order rate model. As changing the PVP/AAc composition from 30/70 to 80/20, the capacity of the composite to bind copper ions increased from 2 to 23 mg/g. The greatest uptake for Fe^{3+} and Mn^{2+} is 36 and 14 mg/g, respectively.

Wet and soft hydrogel materials have low mechanical strength. In order to maintain a good mechanical property, water-soluble monomers can be grafted onto some readily available commercial materials with high mechanical strength (such as poly(ethylene terephthalate) (PET) fibers) [Karakisla 2003, Coskun 2006]) or some natural materials [Shibi 2002 and 2005].

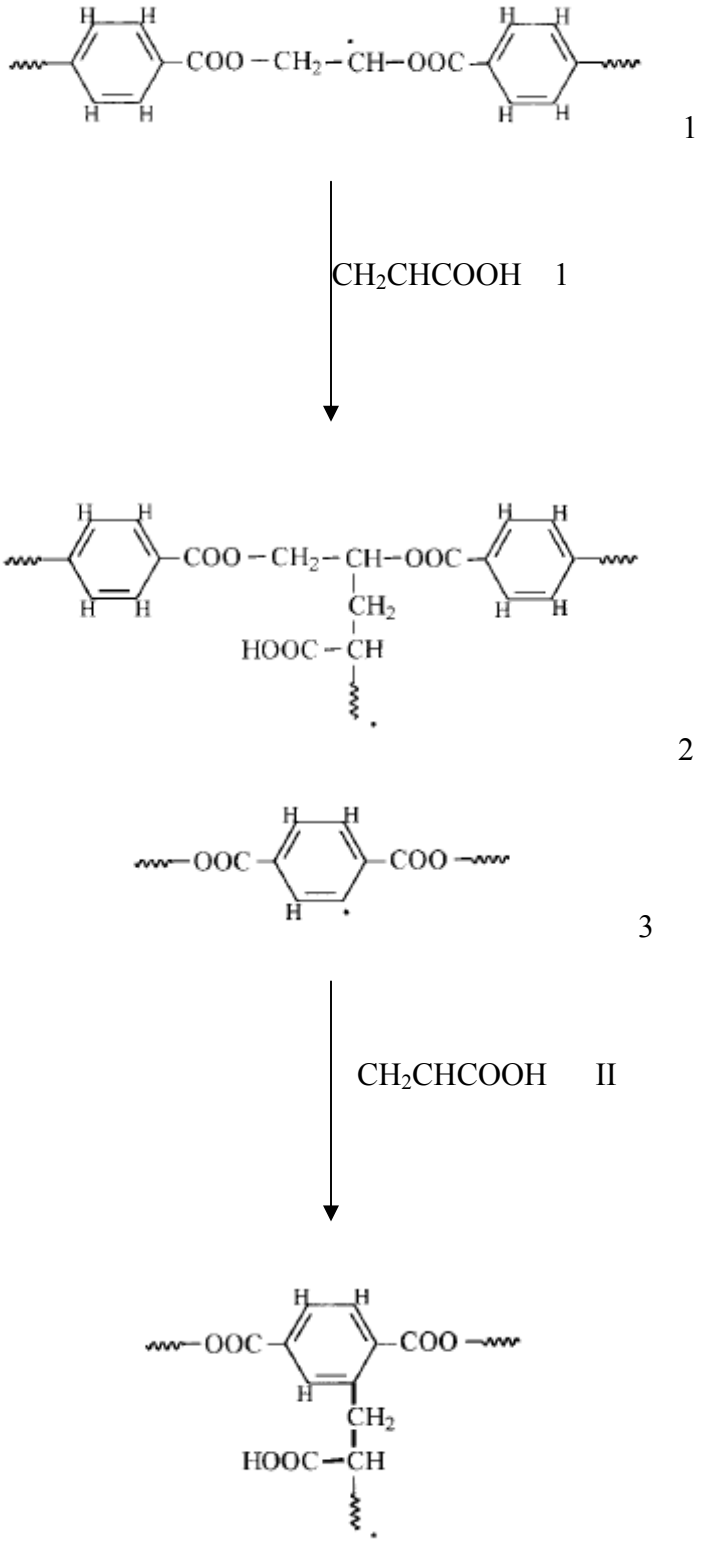

Figure 2- 9 Reaction mechanism of monomer grafted onto PET [Campbell 1970]

PET fiber is a commonly used synthetic material. When acrylic acid, acrylamide and their derivatives are grafted onto PET fibers, a water-absorbing material with high mechanical properties can be obtained. Using Bz_2O_2 as an initiator, a water-absorbing material product can be produced by surface grafting shown in Figure 2-9. There are two radical reactive sites on ethylene terephthalate which can propagate the grafting reaction. Campbell [1970] found the type II radical site on PET to be predominant. Thus, the water-soluble monomers were mainly grafted onto PET according to type II reaction mechanism to produce product 4.

When the grafting monomer is acrylic acid, increasing pH from1 to 6 will increase copper uptake. The copper ions sorption isotherm follows Langmuir model, and the sorption kinetics can be well described by the Pseudo-first order equation [Karakisla 2003]. At a grafting yield of 13.2 %, the sorption capacity of the hydrogel is about 1.7 mmol/g at pH 5 at 25 ^{o}C.

If other water-soluble monomers such as methacrylic acid and acrylamide were grafted, the hydrogels possess strong sorption capacities for metal ions. The sorption capacity for Cu^{2+}, Ni^{2+} and Co^{2+} was reported to be 31.25, 43.48 and 27.1 mg/g, respectively [Coskun 2006]. Competitive adsorption tests suggested sorption selectivity for Cu^{2+} with the coexistence of Co^{2+} and Ni^{2+}. The sorption isotherm and kinetics follow Langmuir model and pseudo-first order equation, respectively. In addition, it was also found that when the grafting yield increases from 10 to 130 %, the sorption capacity increases sharply. With an increase in pH from 2 to 6, the sorption capacity for metal ions increases sharply.

It is a relatively new approach to prepare sorbent by grafting water-soluble monomers onto natural materials [Shibi 2002 and 2005]. Banana stalk, a kind of lignocellulose, can be used as a hydrogel matrix, and acrylamide monomer can be grafted onto its backbone. Using ferrous ammonium sulphate/H_2O_2 as a redox initiator system, solid phase grafting was carried out at 70 ^oC for 4 hours, as shown in Figure 2-10. The solid sorbent can remove heavy metal ions (Hg^{2+} and Co^{2+}) from aqueous solutions. The sorption experimental data showed the sorption kinetics and isotherm can be described by pseudo-second-order kinetic equation and Freundlich model, respectively. It is important to note that Co^{2+} state is dependent on pH. Below a pH of 6, most cobalt ions (II) exist in the state of Co^{2+} ions in the solution. At a higher pH, $Co(OH)^+$ and $Co(OH)_2$ begin to appear in the soluion, but the Co^{2+} ions gradually diminish. A further increase of pH to 10 will cause $Co(OH)^+$ to decline and above pH 11, Co^{2+} and $Co(OH)^+$ finally disappear and only $Co(OH)_2$ exists in the solution.

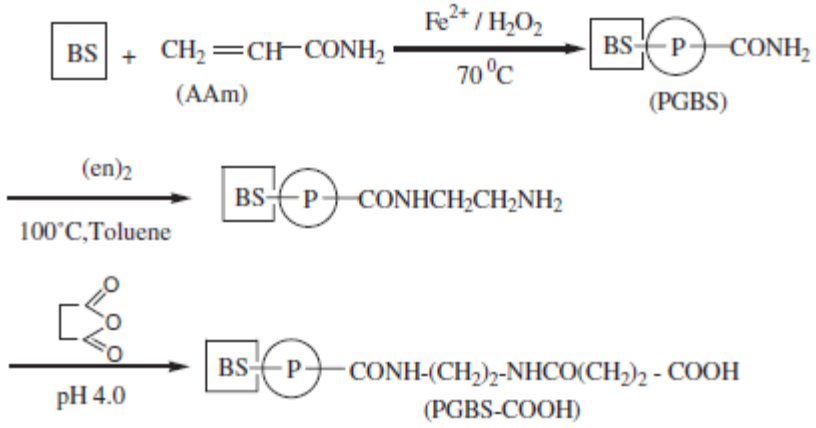

Figure 2- 10 Preparations of polyacrylamide-grafted banana stalk (PGBS-COOH) [Shibi 2002 and 2005].

Chitosan, (Figure 2-11) is another natural material with a strong sorption capacity for metal ions. Acrylic acid was grafted onto chitosan beads to functionalize its surface by Li [2006] using a two-step process shown in Figure 2-12. Chitosan granules were prepared first. A homogeneous chitosan solution in acetic acid (2 %, w/w) was injected in droplets into a 1 M NaOH solution to form chitosan beads. The beads were then cross-linked by ethylene glycol diglycidyl ether (EGDE) solution at 70 °C for 6 h. The cross-linked chitosan beads obtained were washed with water until a pH 6-6.5. These beads had an average size of about 1 mm. Then, PAAc was graft onto the chitosan beads. A solution containing PAAc and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (WSC) was used to graft PAAc on the chitosan beads at 4 °C for 24 h. The beads were then separated from the solution and washed with deionized water to remove any unreacted or loosely bound PAAc. The resulting beads were used to remove Pb^{2+} ion at a pH range of 1-6. Comparing with the adsorption capacity (95.15 mg/g) of pure chitosan, the sorption capacity of the PAAc-chitosam composite was increased sharply to 294.12 g/g. Among the Langmuir, Freundlich and Temkin sorption isotherm models, the Langmuir model was shown to work best. The sorption kinetics was shown to follow the pseudo-second-order kinetic model.

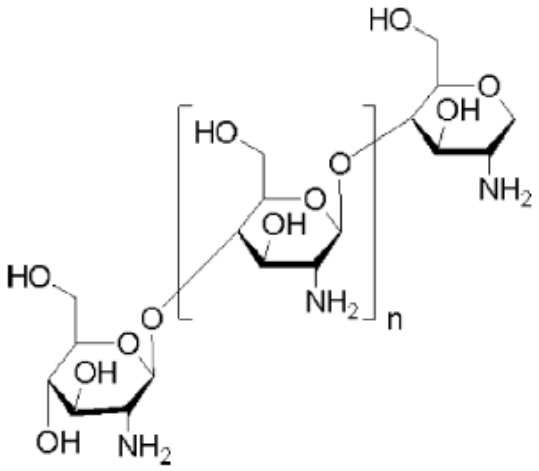

Figure 2- 11 Molecular formula for Chitosan [Zhao 2004]

Water soluble monomers and chitosan can also be used to prepare interpenetrating network (IPN) composites. A simple and facile method to prepare a composite of a chitosan and water soluble molecules for metal ion adsorption is to directly polymerize acrylamide in chiosan suspension [Akkaya 2008]. Firstly, chitosan was suspended in water to form a homogeneous suspension. Then, a solution containing acrylamide monomers was added to the suspension and stirred. Cross-linking agent, (N, N'-methylenebisacrylamide) and initiator (ammonium persulphate and N,N,N',N'-tetramethylethylenediamine) water solution were added to the suspension. The polymerization was carried out at 25 °C, and the PAAc–Chitosan gel was washed with distilled water until the effluent attained a neutral pH. This hydrogel was used to adsorb Pb^{2+}, UO_2^{2+}, and Th^{2+}. Compared to pure chitosan, the composite of chitosan and polyacrylamide with interpenetrating network has an improved binding for UO_2^{2+} and Th^{2+}. Among the entire isotherm models (Langmuir, Freundlich and Dubinin-Radushkevich) tested to describe the experimental data, the Langmuir model appeared to

give a more reasonable result. In addition, the composite had a higher adsorption rate for UO_2^{2+} and Th^{2+} than chitosan.

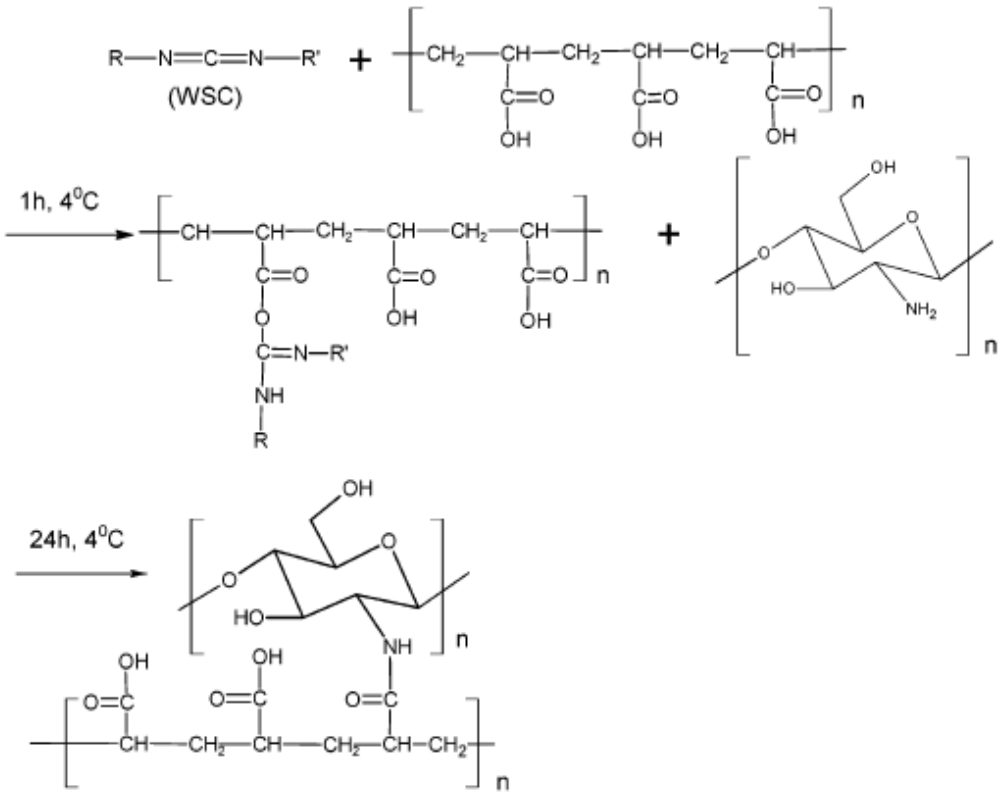

Figure 2- 12 Two-Step process for poly(acrylic acid) grafting on chitosan beads [Li 2006].

Clay is a common inorganic filler in composite preparation. A clay/poly(methoxyethyl)acrylamide (PMEA) composite was prepared by bulk polymerization for Pb^{2+} removal from aqueous solutions [Solener 2008]. At first, the monomer was initially dissolved in deionized water, and then clay was added and mixed using a magnetic stirrer. An aqueous solution of the cross-linking agent *N*, *N*-methylenebisacrylamide (MBA) was added at 4°C. Subsequently, an aqueous potassium

persulfate (KPS) solution and an aqueous solution of tetramethylethylenediamine (TEMED) were added as initiator and accelerator, respectively. The container was placed in a water bath at 4°C, mixed with a magnetic stirrer, and a clay–polymer composite formed in 30 min. Then, the reactor was preserved in a water bath at 4°C for 24 h, followed by washing with deionized water at 4°C for 2 h to rinse unreacted monomers and initiator components completely. Finally, the clay–polymer composite was dried under vacuum at 50°C for 48 h. The capacity of the composite for Pb^{2+} sorption increased from about 1 to over 30 mg/g when the pH increased from 1 to 6. The adsorption kinetics followed a pseudo-second-order kinetic model, and the Dubinin-Radushkevich model was found to be satisfactory to describe the sorption isotherm.

Many proteins in nature can sequester submicromolar concentrations of heavy metal ions (Cu^{2+}, Zn^{2+}, Ca^{2+}, Hg^{2+}, Cr^{2+}, Ni^{2+}, Pb^{2+}) in aqueous solutions [Schwarzenbach 2006]. They are attracting significant attention in water treatment due to their strong metal binding capacity and high selectivity. Protein-polymer hybrid composite materials have been reported as hydrogel adsorbent to remove heavy metal ions from water solution [Gilmore 2006, Esser-Kahn 2008A and 2008B]. In the composites, the macromolecular chain acts as the backbone of the hydrogel material, and the protein molecules function as only a cross-linking agent. The compatibility between protein and polymer is not strong enough and may result in phase separation. Thus, a reactive ketone group can be introduced at the N- and C- terminal of a selected protein (peptide) chains. The functional groups in the protein can react with the functional groups in the polymer chains to form a linkage between protein and macromolecule. The composite has a heterogeneous structure. In general, the polymers used are based on acrylamide and its

derivatives. They are prepared by radical polymerization. Alkoxyamino-substituted acrylamide monomer was also employed [Gilmore 2006, Esser-Kahn 2008B]. The protein-cross-linked hydrogel and the mechanism for sequestration of heavy metal ions are shown in Figure 2-13. When binding heavy metal ions, the protein molecules contracts and the volume of the hydrogel decreases. The capacity of the composite materials for binding metal ions is shown in Figure 2-14, and they have a high removal capacity for Hg^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, and Co^{2+}.

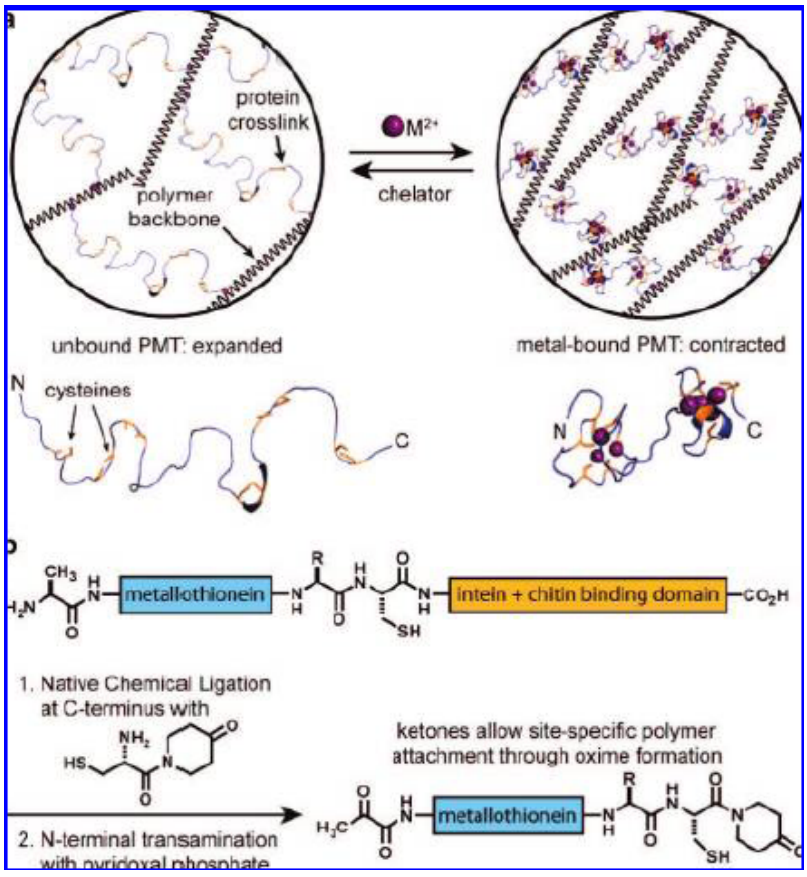

Figure 2- 13 Protein-cross-linked hydrogel for sequestration of heavy metal ions [Esser-Kahn 2008A]

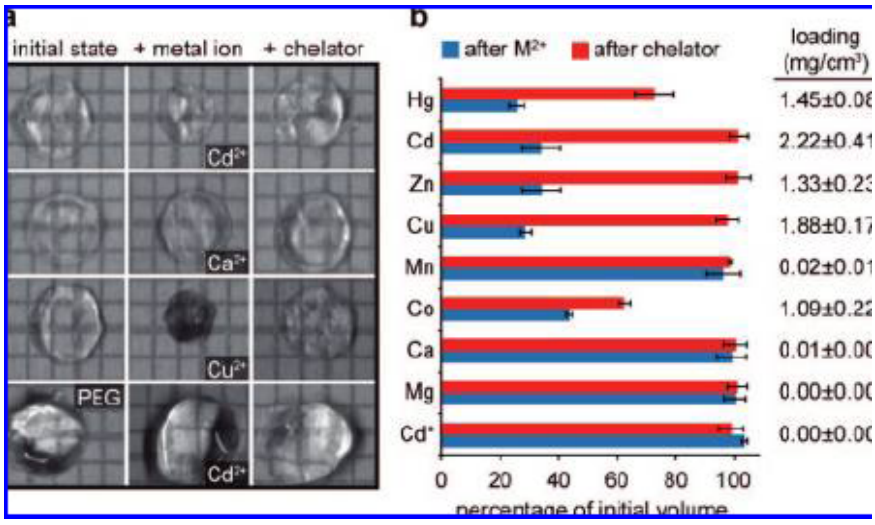

Figure 2- 14 Data and images of hydrogel for sequestration of heavy metal ions [Esser-Kahn 2008A]

2.3 Adsorption mechanism

Both linear poly(acrylic acid) and cross-linked poly(acrylic acid) are hydrophilic because of the carboxyl groups in the macromolecular chains. The polymeric acid (which is a polyelectrolyte) can dissociate to give H^+ and carboxyl anion, $-COO^-$ in an aqueous solution. When metal ions (e.g. Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ca^{2+}, Mg^{2+}) were added into the polymeric acid solution, because the polymeric acid can associate with these metal ions, the dissociation equilibrium will be influenced by metal binding at a given concentration of metal ions. A great deal of work has been done to investigate the interaction between poly(acrylic acid) and metal ions [Gregor 1955, Masaaki 1979, Yokoi 1986, Benegas 1998, Porasso 1999, Tomida 2001, Rivas 2005, Huang 2007].

According to the modified Bjerrum model [Bjerrum 1941, Gregor 1955, Tomida 2001], the complexes of poly(acrylic acid) and divalent metal ions can successively form various complexes in an aqueous solution, and the equilibrium can be described by:

$$HL + M^{2+} \Leftrightarrow LM^{+} + H^{+}; K_1 \tag{2-5}$$

$$HL + LM^{+} \Leftrightarrow L_2M + H^{+}; K_2 \tag{2-6}$$

where K_1 and K_2 are successive stability constant.

If one single metal ion coordinates more than two ligands (carboxyl groups) of the poly(acrylic acid), the complex equilibrium can be expressed as:

$$nHL + L_2M \Leftrightarrow L_2M(HL)_n; K_n \tag{2-7}$$

where K_n is a stability constant.

The successive constants for the above three equilibrium can be giving by:

$$k_1 = \frac{[LM^{+}][H^{+}]}{[HL][M^{2+}]} \tag{2-8}$$

$$k_2 = \frac{[L_2M][H^{+}]}{[HL][LM^{+}]} \tag{2-9}$$

$$k_{\mathrm{n}} = \frac{[L_2M(HL)_n]}{[HL]^n[L_2M]} \tag{2-10}$$

where HL is the functional groups in the macromolecular ligands, M^{2+} is the divalent ion. LM^+, L_2M and $L_2M(HL)_n$ are the complexes.

As for polymeric acid ligands, the dissociation equilibrium constant of the carboxyl groups at a given metal ion concentration can be given by [Gregor 1955, Tomida 2001]:

$$K_a = [H^+](\frac{[L^+]}{[HL]})^{\beta} \tag{2-11}$$

where β is a constant related to metal ions.

The relationship among the pH, dissociation equilibrium constant (K*a*) and the α can be expressed by the modified Henderson-Hasselbach equation (2-12). α is the degree of polymer acid neutralization, expressing the molar ratio of sodium hydroxide to the carboxyl groups in the macromolecular ligands. It can be expressed by the equation (2-13) [Gregor 1955, Porasso 2000, Tomida 2001].

$$pH = pK_a - \beta \log(\frac{1-\alpha}{\alpha}) \tag{2-12}$$

$$\alpha = ([NaOH] + [H^+] - [OH^-]) / C_p \tag{2-13}$$

where [NaOH] is the concentration of the added sodium hydroxide solution, Cp is the total poly(acrylic acid) concentration (carboxylic and carboxylate groups).

A complex of poly(acrylic acid)-divalent metal ion is illustrated in Figure 2-15. This complex shows a tetrahedral structure (square planar complex) [Tomida 2001].

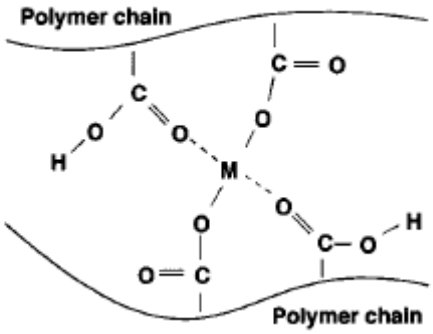

Figure 2- 15 The structure for poly(acrylic acid)-divalent metal ion complexes of $L2M(HL)_2$ [Tomida 2001]

According to the above-mentioned analysis, sodium hydroxide can directly influence the pH of the solution, and α and the state of carboxyl groups, and eventually affects the coordination number of functional groups in the macromolecular ligands and the amount of metal binding.

The average coordination number of poly(acrylic acid)-metal ion complexes depends on the pH (4-6) of the aqueous solution and the molar ratio of carboxyl groups to the metal ions. It can vary from 0 to more than two [Tomida 2001]. For divalent copper ion, at a pH of 4, when the equilibrium concentration of copper ions increases from 0 to 1 mM, the average coordinate number decreases from 3.5 to 2. At a pH of 5, the number of

the average coordinates changes from 2 to around 1.5 with increasing the equilibrium concentration of copper ion from 0 to 1 mM. This result shows that with an increase in equilibrium concentration of metal ions in the solution and pH, the complexes with one or two ligands are predominant.

With respect to the coordination number and the state of the metal ions (Cu^{2+}) in a broader pH range from less than 3 to over 9, Yokoi [1986] reported the following results: there are two factors determining the status of Cu^{2+} in an aqueous solution. One is the pH of the solution and the other one is the ratio of the residual functional groups in poyl(acrylic acid) to Cu^{2+} concentration. If pH is less than 3, the copper ions can exist as ordinary hydrated Cu^{2+} in aqueous Cu^{2+}-poyl(acrylic acid) solutions, and no copper ion complexes can be formed. In a pH range of 3-8, mononuclear complexes of copper ions with one (ML) or two (ML_2) carboxyl groups from poyl(acrylic acid) can be formed in an aqueous solution. The coordination of copper ions to carboxyl groups in poyl(acrylic acid) is strain-free. At a pH below 4, (ML) is the preferential complex. Furthermore, when the ratio of carboxyl groups to copper ions is relatively low (≤ 10), a large amount of binuclear copper (II) complexes can be formed at pH 4. When the pH raises further to 9, all mononuclear and binuclear complexes of Cu^{2+} finally disappear.

It is worthy of noting that when the pH increases to 6, inorganic compound $Cu(OH)_2$ can be gradually formed. However, because of a high local concentration of carboxyl groups and a polyelectrolyte field effect, $Cu(OH)_2$ does not precipitate in the aqueous solution but remains in the solution due to hydrophilic interaction with poyl(acrylic acid). Therefore, in the range of solution pH 4-7, the water-sorption and metal binding capacity

of the hydrogel copolymers increases with an increase in pH [Yokoi 1986, Tomida 2001] due to formation of mononuclear and binuclear metal (Cu^{2+}) ion complexes.

As stated before, it is a complicated process for metal ion to associate with such macromolecular ligands as poly(acrylic acid). The apparent dissociation constant, *Ka,* is influenced by not only the counter ions but also the flexibility of the polymer ligands [Porasso 1999 and 2000]. According to the counter ion condensation theory, the change of the apparent dissociation constant involves electrostatic interactions between the metal ions and the polymer ions and chemical binding of counter ions of different valence. The total free energy for carboxyl groups in poyl(acrylic acid) binding metal ions can be considered to consist of contributions from electrostatic and entropic mixing contributions. The bound fraction of metal ions leads to a decrease in charge of poly(acrylic acid) by a fraction σ, which reduces the electrostatic interaction between carboxyl groups and metal ions in the solution. With an increase in chemical binding, more negative value of the intrinsic free energy of binding is obtained resulting in a high binding capacity.

Poly(acrylic acid) can also bind metal ions in solid state even though most water molecules were removed from solution [Yoon 2005]. Linear poly(acrylic acid) (MW=240 000) in an aqueous solution (25 wt %) containing metal ions was spin-coated on a surface of a α-Al_2O_3 single crystal to form a thin film. The solution pH was adjusted by 1M NaOH and 1 M HCl. By using Long-Period X-ray Standing Wave Fluorescent Yield (XSW-FY) and X-ray reflectivity techniques, the partition result of metal ions (Pb^{2+} and AsO_4^{3-}) was determined between the poly(acrylic acid) film and the metal oxide. It was

reported that the metal ions were preferentially bound by the poly(acrylic acid) film even though the concentration of metal ions (Pb^{2+}) was very low.

CHAPTER 3 EXPERIMENTAL

3.1 Materials

The monomers acrylic acid (AAc, 99 %) and acrylamide (AAm, 99%) were obtained from Sigma, and used without further treatment. Ammonium persulfate (APS, 98%), sodium metabisufite (98%) were used as initiator and accelerator in this study, respectively. They were purchased from Sigma and Fluka, respectively. Sodium hydroxide (99%) was provided by Riedel-Dehaen. Cross-linker *N, N*-Methylenebis(acrylamide) (MBA, 99.5%) was also provided by Fluka. $CuSO_4$ was obtained from Sigma. All other chemicals used were of analytic grades. Figure 3-1 shows the molecular formula of the co-monomers, cross-linking agent, initiator and accelerator.

3.2 Synthesis of copolymer hydrogels

Cross-linked copolymers of acrylamide and acrylic acid (sodium acrylate) were prepared by free radical polymerization using monomers acrylamide and acrylic acid (sodium acrylate) and cross-linking agent N, N-methylenebisacrylamide (MBA). A redox initiating system, consisting of ammonium persulfate and sodium metabisuffite, was used as an initiator. A 1.25 M solution of acrylic acid was prepared, and 75 % of carboxyl groups were neutralized using sodium hydroxide at room temperature, that is, 75 % of acrylic acid was transformed to sodium acrylate. A 1.25 M solution of acrylamide was also prepared. At first, a predetermined amount of cross-linking agent (MBA) was put into a 50 ml beaker, followed by adding a fixed volumes of the prepared acrylic acid

(sodium acrylate) (1.25M) and acrylamide (1.25M) solution. The mixture was mixed thoroughly in the beaker to form a clear solution. Subsequently, 1.0 ml of initiator (APS) solution (0.1M) was injected into the beaker using a syringe. Oxygen dissolved in the solution from air was purged out by bubbling pure nitrogen gas through the solution for 10 minutes at room temperature. Then, 1.0 ml of accelerator (sodium metabisufite) (0.1M) was added into the solution, followed by nitrogen gas purging for 5 minutes. The beaker was enclosed into a plastic bag filled with pure nitrogen gas for blanketing the reaction mixture. Finally, the reaction mixture and the plastic bag were moved into an oven at 45 °C for about 4 hrs to allow polymerization and the hydrogel. Figure 3-2 shows the synthesis of the copolymers of acrylic acid (sodium acrylate) and acrylamide. Table 3-1 summarizes the compositions of the reaction mixtures and the designation of the polymer samples produced.

The hydrogel copolymers obtained were broken into small sizes and immersed in deionized water for more than one week to remove the water-soluble residual monomers and linear copolymers. The copolymer samples were then dried in an oven at 60-80 °C and then further dried under vacuum at 60-80 °C until a constant weight of the sample was established. The obtained sample was a white powder.

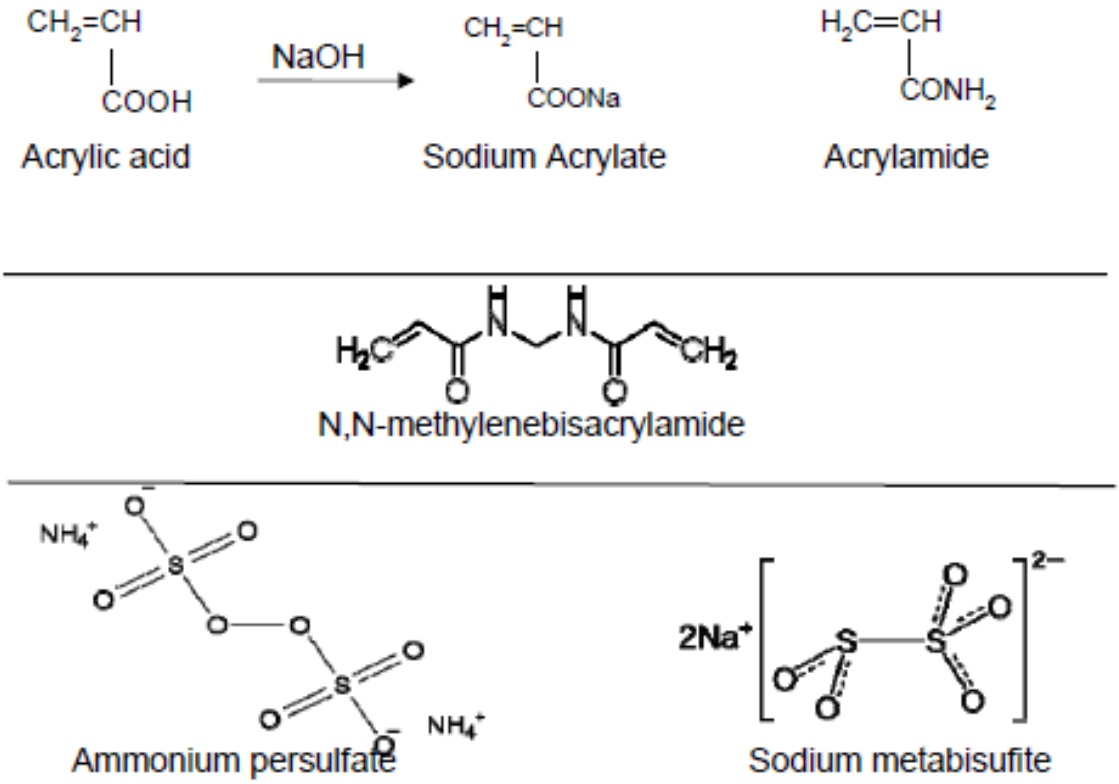

Figure 3- 1 Molecular formula of the co-monomers, cross-linking agent, initiator and accelerator.

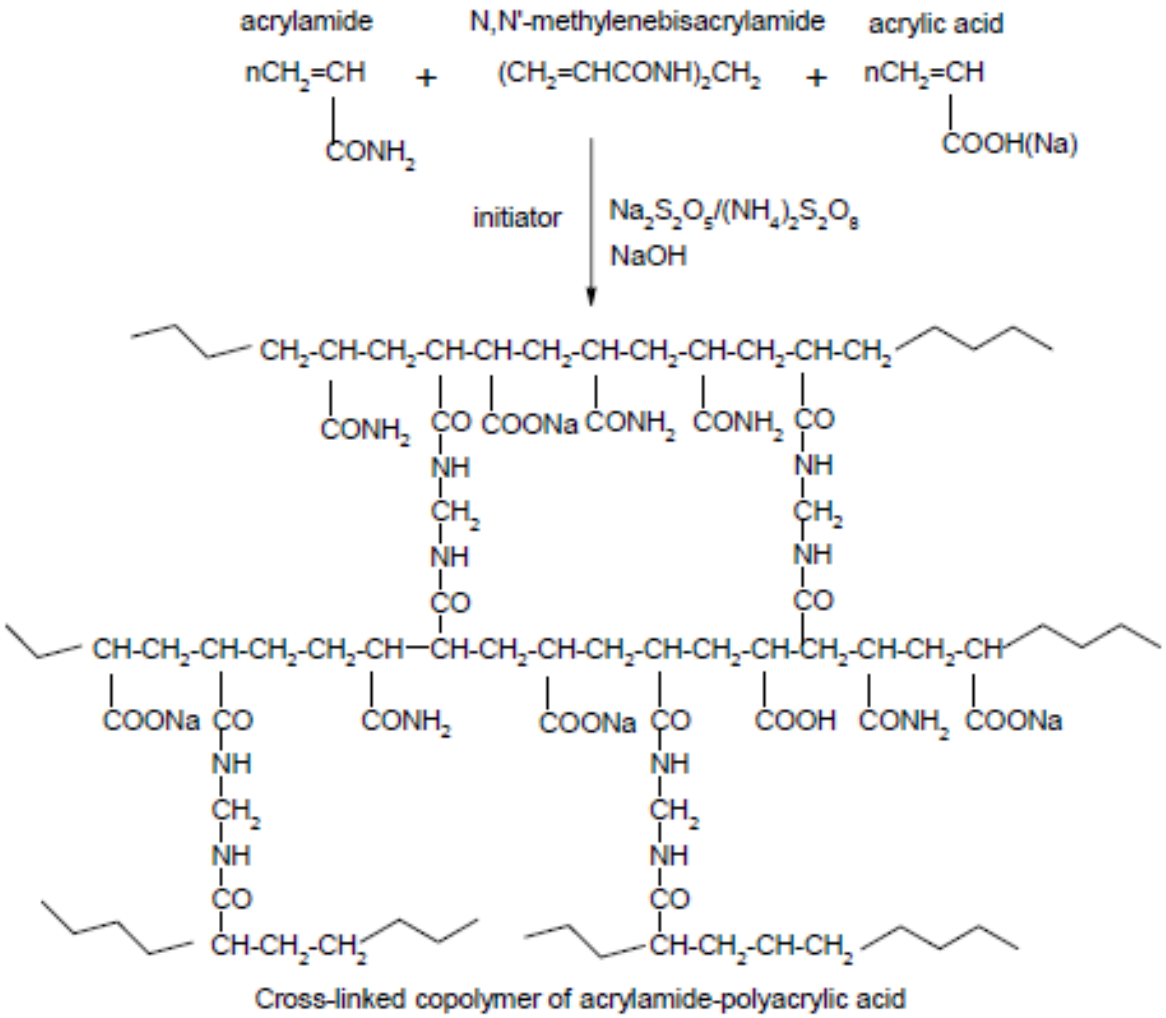

Figure 3- 2 Synthesis of copolymers of acrylic acid and acrylamide.

Table 3- 1 Chemical composition of hydrogel samples prepared in aqueous solution

Set	Sample	AAc mol %	AAm mol %	MBA mol %	APS (Na) mol %
1	1-1	100	0	1	0.2
	1-2	100	0	2	0.2
	1-3	100	0	3.9	0.2
	1-4	100	0	7.4	0.2
	1-5	100	0	13.8	0.2
2	2-1	80	20	1	0.2
	2-2	80	20	2	0.2
	2-3	80	20	3.9	0.2
	2-4	80	20	7.4	0.2
	2-5	80	20	13.8	0.2
3	3-1	60	40	1	0.2
	3-2	60	40	2	0.2
	3-3	60	40	3.9	0.2
	3-4	60	40	7.4	0.2
	3-5	60	40	13.8	0.2
4	4-1	40	60	1	0.2
	4-2	40	60	2	0.2
	4-3	40	60	3.9	0.2
	4-4	40	60	7.4	0.2
	4-5	40	60	13.8	0.2
5	5-1	20	80	1	0.2
	5-2	20	80	2	0.2
	5-3	20	80	3.9	0.2
	5-4	20	80	7.4	0.2
	5-5	20	80	13.8	0.2
6	6-1	0	100	1	0.2

	6-2	0	100	2	0.2
	6-3	0	100	3.9	0.2
	6-4	0	100	7.4	0.2
	6-5	0	100	13.8	0.2

Monomer concentration (AAc+AAm): 1.25M

Amount of initiator: 0.2 mol %, based on total amount of monomers

Amount of MBA: mol %, based on total amount of monomers

Polymerization temperature: 45^{o}C

AAc: Acrylic acid

AAm: Acrylamide

MBA: *N, N*-Methylenebis(acrylamide)

APS : Ammonium persulfate

Na: Sodium metabisufite, accelerator, same quantity as APS

3.3 Adsorption experimental

3.3.1 Water adsorption

The polymer samples were tested for water sorption. The polymer samples were ground to fine powders. 0.500g of the sample was then placed in a beaker containing a pre-determined volume of deionized water. The water sorption was allowed to occur for at least 3-days at room temperature to reach equilibrium. The swollen hydrogel was filtered and weighed. Then, the hydrogel was dried under vacuum at 80^{o}C until a constant weight was attained.

The water sorption uptake, S_W (g/g), was determined gravimetrically:

$$S_W = \frac{m_w - m_0}{m_0} \tag{3-1}$$

where m_w is mass of swollen gel at sorption equilibrium (g), and m_0 is the mass of the dry polymer (g).

3.3.2 Copper uptake from aqueous $CuSO_4$ solutions

Dry powder samples (0.100 g unless specified otherwise) were immersed in 50.00 g of a copper sulfate solution at given concentrations. The sorption equilibrium was attained after 3 days at room temperature (23 ^oC), and the samples were filtered and weighed.

The total sorption uptake (including $CuSO_4$ and water), S_{sol} (g/g), was determined from:

$$S_{sol} = \frac{m_s - m_0}{m_0} \tag{3-2}$$

where m_s is the mass of the hydrogel in $CuSO_4$ solution at sorption equilibrium (g), and m_0 is the mass of the dry polymer (g).

Considering that water was also adsorbed by the copolymer hydrogels, to further determine the copper ion (copper sulfate) uptake, the copper ion concentrations in the original solutions and in the solutions at sorption equilibrium was measured using inductively coupled plasma (ICP) spectrophotometer (Thermo Jarrell Ash; Model: ICP

61E). An Atomic Emission Spectroscopy (AES) detector was used, whose detection limit is 0.02 mg/l for Cu^{2+} and 0.5 mg/l for Na^{+}. Every sample was measured at least three times, and the average number was used as the data for the sample.

It was noticed that when copper ions (II) were taken up by the copolymer sorbent, some sodium ions were released to the liquid. The following equations were applied to calculate the sorbed amount of Cu^{2+}, $CuSO_4$, and water as well as Na^{+} loss per unit weight of dry polymer:

$$S_{Cu}(mmole/g) = \frac{m_{sol-o}C_{0Cu} - (m_{sol-o} - m_{sol-a})C_{e\,Cu}}{m_0\rho} \tag{3-3}$$

$$S_{CuSO_4}(g/g) = \frac{159.6}{1000}S_{Cu} \tag{3-4}$$

$$S_W(g/g) = S_{Sol} - S_{C_uSO_4} \tag{3-5}$$

$$S_{Na}(mmole/g) = \frac{(m_{sol-0} - m_{sol-a})C_{eNa}}{m_0\rho} \tag{3-6}$$

where S_{Cu} is copper ion uptake (mmol/g) per unit dry copolymer sample, S_{CuSO4} is copper sulfate uptake (g/g), S_W is water sorption uptake (g/g), S_{Na} is sodium ion loss (mmol/g), m_0 is mass of dry polymer samples (g), C_{0Cu} is copper ion concentration in original solution (mM), C_{eCu} is copper ion concentration (mM) in solution at equilibrium, C_{0Na} is sodium ion concentration in original solution (mM) (should be 0), C_{eNa} is sodium ion concentration in solution at equilibrium (mM), m_{sol-0} is original mass of solution (mg),

$m_{sol\text{-}a}$ is mass of solution (mg) sorbed in hydrogel. The density (ρ) of the dilute solution is considered to be the same as density of pure water (g/ml).

The percentage (P %) of copper ions captured by the copolymer hydrogels, i.e. the percentage of the bound copper ions accounting for total amount of copper ions, is given by:

$$P,\% = \frac{C_{0Cu} m_{sol-0} - (m_{sol-0} - m_{sol-a}) C_{eCu}}{C_{0Cu} m_{sol-0}} \times 100\% \qquad (3\text{-}7)$$

3.4 Sorption isotherm

To study the sorption isotherm, a copolymer of 80 mol % acrylic acid (75 % of carboxyl groups in the acrylic acid were neutralized by sodium hydroxide) and 20 mol % acrylamide was used in the experiment. The cross-linking agent (MBA) is 3.9 mol % based on the total quantity of the co-monomers.

The experimental procedure for sorption tests was the same as described above, except that the copper concentration was varied over a wide range from 0 to 2300 ppm (36.22 mM).

3.5 Qualitative observation on copper adsorption

An irregular piece of the copolymer sample was immersed in deionized water in a beaker. This copolymer was synthesized from 40 mol % AAm and 60 mol % AAc (75 % AAc was neutralized with sodium hydroxide), and the content of the cross-linking agent (MBA) was 2 mol % based on the total quantity of co-monomers. In order to remove the

linear (co)polymers and the residual monomers, the hydrogel sample was rinsed at least three times with fresh deionized water. When sorption equilibrium was established (in about one week), the hydrogel sample was picked up and weighed. Afterward, the water-sorbing hydrogel sample was transferred into another beaker containing copper sulfate solution (500ml). The water molecules in hydrogel start to run away from the copolymer hydrogel. When a new sorption equilibrium was reached (in three days), the sample was taken out from the beaker. After removing the water solution on the surface of the sample, its weight was measured. Then, the sample was transferred into another beaker containing a copper sulfate solution with a higher concentration. The above-mentioned procedure was repeated. A series of experiments was performed using different copper sulfate concentrations.

3.6 Wide Angle X-ray Diffraction (WAXD) characterization

Hydrogel samples were immersed into a copper sulfate solution (1396 ppm or 21.98 mM) for about 7-days at room temperature. The hydrogel sample was taken from the solution and surface water removed. Afterward, the wet hydrogel copolymer was oven-dried at 80 ^{o}C, and then dried under vacuum at 80 ^{o}C to remove residual water. The dried samples were ground to fine powders. The powder samples were examined using wide angle X-ray diffraction (WAXD). For comparison purpose, the crystalline structure of pure $CuSO_4$ was also examined. A Bruker (Bruker D8-Focus) diffractometer was employed in these experiments. The X-ray wavelength was 1.5418 Å, and the scattering angle, 2 θ, was examined from 0 and 50^{o} with 0.1^{o} intervals. The WAXD plots were

fitted, and smoothed by using Origin software. The sample used was a copolymer of AAc (60 mol %) and AAm. 75 mol % carboxyl group in the AAc chain was neutralized with sodium hydroxide. The content of cross-linking agent (MBA) was 2 mol % based on the total amount of the co-monomers.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Adsorption

Cross-linked copolymers of acrylic acid (partially neutralized) and acrylamide were synthesized by radical polymerization in aqueous solutions. These soft and wet hydrogel materials can easily swell in aqueous solutions due to the hydrophilic groups in the macromolecular chain. However, they are not soluble in water. These materials showed different sorption capacity for pure water and metal uptake. Copper sulfate was used as a model adsorbate in this research.

4.1.1 Pure water sorption

Figure 4-1 shows the results of pure water sorption as a function of macromolecular structure of cross-linked copolymers. In this three-dimensional chart, the two horizontal axes show the content (mol %) of acrylic acid (sodium acrylate) in the co-monomers and the content (mol %) of cross-linking agent (MBA) used in the copolymer synthesis, respectively, and the longitudinal axis indicates the water sorption uptake.

It can be seen that the water sorption capacity (g/g-copolymer) of the hydrogel sample increases when the content of the acrylic acid (sodium acrylate) in the co-monomers increased. This trend becomes more significant at a higher content of the acrylic acid (sodium acrylate). On the other hand, with an increase in the content of the cross-linking agent, the above-mentioned phenomenon (water sorption increasing with an increase in acrylic acid content) becomes more apparent. A maximum sorption uptake of

about 820 g/g is attained with polymer produced from only acrylic acid at 1.0 mol % cross-linking agent. Clearly, acrylic acid (sodium acrylate) has a strong influence on the water sorption capacity of the copolymer hydrogels. The carboxyl groups in the acrylic acid (sodium acrylate) exhibit a high capacity for holding water molecules compared to the amide of acrylamide. Similar results have been obtained by Ilmain [1991] and Endo [2001]. When the AAc/AAm composition changes from 0/100 (mole/mole) to 20/80 and from 80/20 to 100/0, the water sorption capacity of the polymers increases dramatically, suggesting that the microstructure of the hydrogel has experienced a big change. This can be attributed to the intermolecular H-bond formed in the hydrogel copolymers [Ilmain 1991, Endo 2001].

As expected, for any given AAc/AAm compositions, a decrease in the content of the cross-linking agent increases the water sorption capacity. The cross-linking affects directly the length of the polymer chain segment and the pore size of the cross-linked network. Increasing the amount of cross-linking agent will result in a higher cross-linking density of the copolymers and smaller sizes of the network pores, which reduces the amount of water that can be accommodated. If the polymers are not adequately cross-linked, although a very large water sorption capacity can be obtained, the resulting hydrogel will be more fragile and difficult to handle due to lack of integrity.

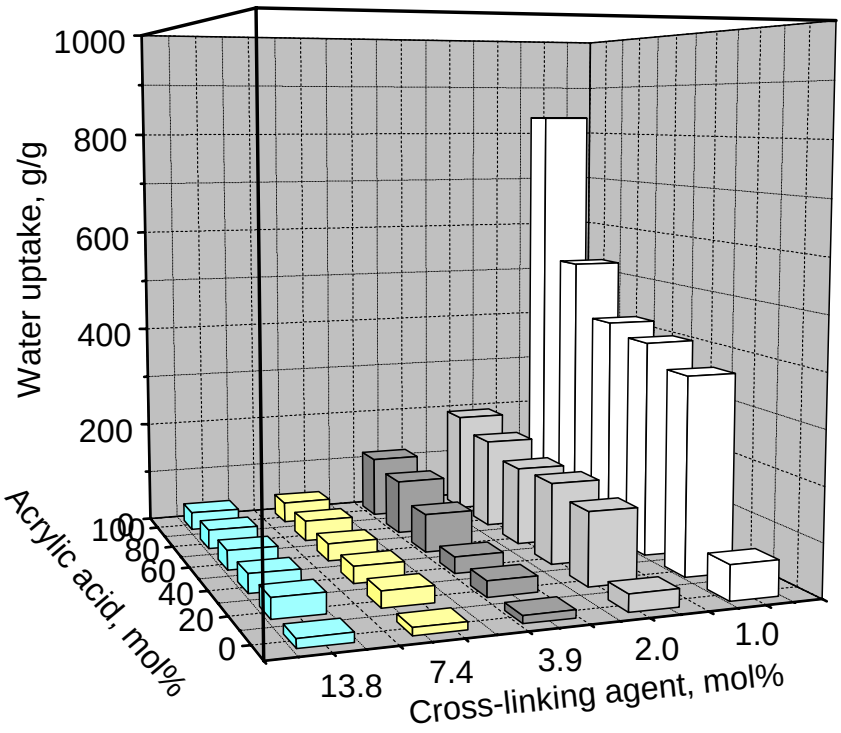

Figure 4- 1 Water sorption uptake of copolymers as a function of co-monomer composition and content of cross-linking agent

4.1.2 Sorption in $CuSO_4$ solution

Adsorption of metal ions from aqueous solutions is an important property of hydrogel materials. The same polymer samples were used in the experiments to test the sorption characteristics of Cu^{2+} ions. The results obtained from these experiments are shown in

Figure 4-2. Compared with pure water sorption, the copolymers have a lower sorption uptake in the copper sulfate solution. At 1300 ppm (20.47 mM) of copper ions in the solution, the total mass uptake (i.e. copper sulfate and water) is only about 5 % of the pure water sorption uptake. In addition, the effect of the copolymer composition on sorption uptake shows a different trend from that of water sorption. At a given content of cross-linking agent, with an increase in the acrylic acid (sodium acrylate) content, the total sorption uptake of the copolymer decreases to a minimum at around 40 mol % of acrylic acid (sodium acrylate) and then gradually increases. The polymer comprising of 100 mol % of acrylic acid shows a maximum sorption uptake. This trend is more significant at a lower content of cross-linking agent. With respect to the effect of cross-linking agent, at a given AAc/AAm composition in the copolymer, the sorption uptake increases with a decrease in the degree of cross-linking. Interestingly, the sorption uptake of copolymers with 40 mol % of acrylic acid (sodium acrylate) is not significantly influenced by the content of the cross-linking agent. However, the effect of cross-linking agent on the sorption uptake becomes more significant when the main component in the copolymer is either acrylic acid or acrylamide.

In this sorption process, the copolymer takes up water molecules and binds copper ions simultaneously. In other words, it is the copper ions that reduce the water sorption uptake in the copolymer hydrogel. The carboxyl groups in the polymers are primarily responsible for the sorption in the copolymer hydrogel. Copper ions have stronger interactions with the carboxyl groups in macromolecular chains than the amide groups. When copper ions are associated with macromolecular ligands, both mononuclear and binuclear copper ion chelate complexes will be formed [Yokoi 1986]. A portion of the

active sorbent sites in the hydrogel copolymer are occupied by copper ions to form chelate complexes [Akkaya 2008,Tsutsui 2006, Katono 1991, Atta 2009] and the chain segments of the copolymers are confined. As a result, the apparent cross-linking density of the copolymers increases, which is equivalent to an increased cross-linking. The pore-size of the copolymer network appears to be smaller. Therefore, the copolymer hydrogel has a lower water uptake in the copper sulfate solution. At a given copper ion concentration, the number of copper ions that can be chelated by carboxyl groups is limited. When the content of acrylic acid (sodium acrylate) co-monomer in the copolymer increases, the carboxyl groups will complex with metal ions preferentially, and the remaining carboxyl groups left as free groups will be the active sites for sorbing water molecules. Therefore, with an increase in the content of the acrylic acid in the copolymer, more carboxyl groups will be available to sorb water molecules. This explains the observation that the water sorption uptake increases with an increase in the content of the acrylic acid in the copolymer. In addition, the amide groups in the copolymer do not form complexes with copper ions and thus do not contribute to metal uptake significantly. However, the amide groups are capable of adsorbing water. The experimental data show that at a given content of the cross-linking agent, the total sorption uptake reaches a minimum when the copolymer contains 40 mol % of acrylic acid (sodium acrylate) and 60 mol % of acryl amide.

In general, longer chain segments tend to have better flexibility and are more beneficial to the formation of the metal chelate complexes. Therefore, the above observations become more apparent as the content of the cross-linking agent decreases.

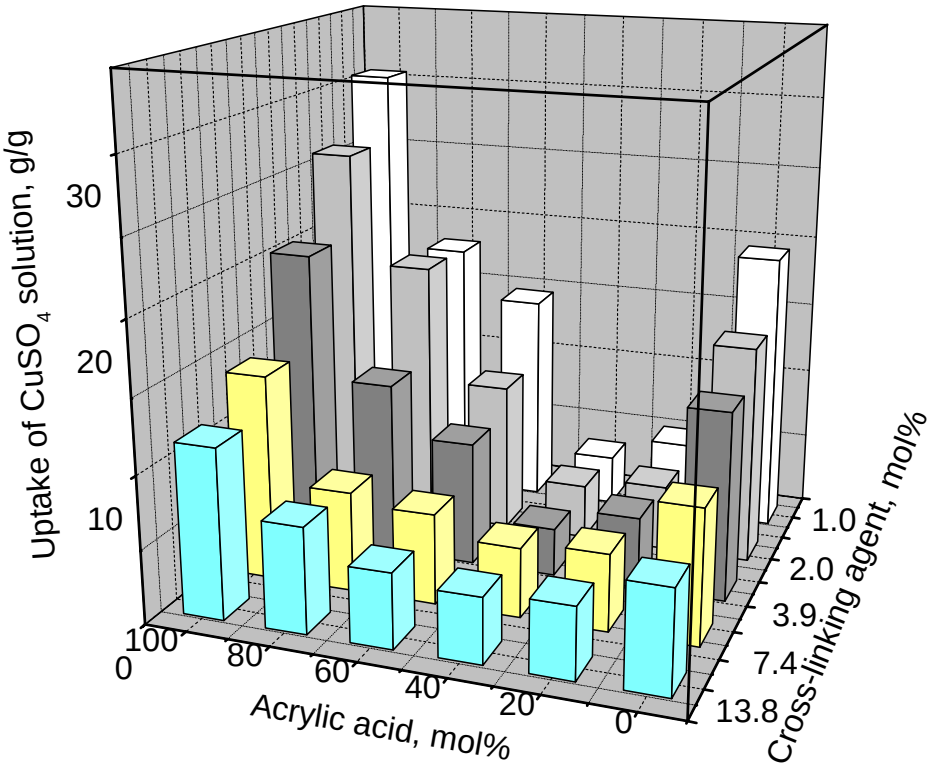

Figure 4- 2 Total sorption uptake (copper sulfate and water) in the (co)polymer adsorbent

Initial conditions of sorption experiment: Copolymer 0.500g, $CuSO_4$ solution 50.00 ml (Cu^{2+}:1300 ppm or 20.47mM). Room temperature.

4.2 Copper ion uptake and water uptake

The total sorption uptake includes water and copper sulfate. In this section, the effect of molecular microstructure of the copolymers (e.g., acrylic acid (sodium acrylate) co-monomer content, percentage of carboxyl groups in AAc neutralized with sodium hydroxide, and content of cross-linking agent) on the copper sulfate uptake and water uptake will be evaluated separately.

4.2.1 Content of acrylic acid co-monomer in copolymer

Carboxyl groups in the copolymers are primarily responsible for the sorption properties of hydrogel materials. In this study, the effects of the density of carboxyl groups and the segment sequence structure on the uptake of copper sulfate and water will be studied. The copolymer of acrylic acid (sodium acrylate) and acrylamide selected for these experiments contained 3.9 mol % of cross-linking agent MBA based on the total quantity of co-monomers. 75 % of carboxyl groups in the acrylic acid co-monomer were neutralized with sodium hydroxide to maintain a pH of about 7.

As described before, with an increase in the acrylic acid (sodium acrylate) co-monomer content in copolymers, the total sorption uptake (including copper sulfate and water) of the hydrogel materials first decreased, and beyond a turning point, the sorption capacity began to increase. Here the sorption uptake of copper sulfate will be separated from water uptake. Figure 4-3 is a plot of copper sulfate uptake and water uptake as a function of the content of the acrylic acid (sodium acrylate) co-monomer in the copolymer. It can be seen that with an increase in the content of the acrylic acid (sodium

acrylate), the copper sulfate uptake increases in a linear fashion. However, the water uptake decreases first and then increases, resulting in a minimum uptake at about 40 mol % acrylic acid (sodium acrylate) in the copolymer. As mentioned before, the carboxyl group, -COOH, has a stronger interaction, than amide group ($CONH_2$), with copper ion [Cavus 2009, Rivas 2004]. Increasing the number of carboxyl groups in the copolymer is expected to increase the mononuclear and binuclear complexes formed. Thus, the copper sulfate uptake gradually increases with an increase in the content of the acrylic acid (sodium acrylate) in the copolymer. However, at a relatively low acrylic acid content in the copolymer, because of the strong chelating complexation, the active sites will be mainly occupied by copper ions, which compete more strongly than water uptake. When the acrylic acid content is above a certain level (i.e., about 40 mol %), the water sorption will gradually increase because of the increased amide groups, which are not affected by metal ion association. The minimum water uptake observed is due to the opposing effects of the acrylic acid (sodium acrylate) and acrylamide on the competitive sorption of $CuSO_4$ and water in the copolymers.

From a macromolecular sequence structure point of view, when the content of the acrylic acid (sodium acrylate) increases from 0 to 20, 40, 60, 80 and 100, the average sequence length of acrylic acid co-monomer (number of acrylic acid co-monomer / number of acrylamide co-monomer) increases from 0 to 1:4, 2:3, 3:2, 4:1, and eventually a sequence of all acrylic acid monomer. For cross-linked copolymers, the average chain segment length between two cross-linking points can be estimated to be 12.8 units. As acrylic acid (sodium acrylate) content increases, the sequence length of acrylic acid (sodium acrylate) co-monomer and carboxyl group density increase. The water sorption

uptake decreases to 1.0 g/g at 40 mol % of acrylic acid (sodium acrylate) content in the polymer from 8.0 g/g in the polymer of 100 % acrylamide, then increases to 2.0 g/g when the polymer contains only acrylic acid (sodium acrylate).

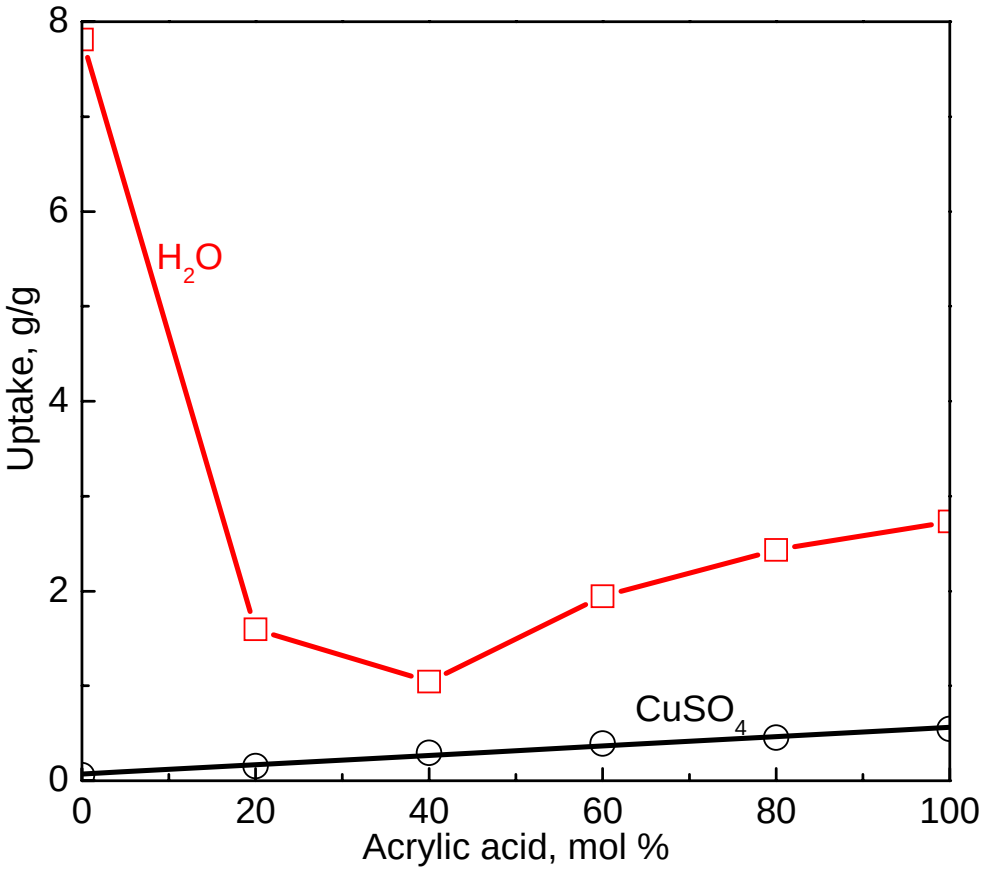

Figure 4- 3 Uptake of water and $CuSO_4$ in the (co)polymers

Copolymer used for this experiment contains AAc (75% carboxyl neutralized with sodium hydroxide), AAm, and 3.9 mol % MBA based on total number of monomers. The initial concentration of copper ion is 1220 ppm (19.21mM).

When the polymer adsorbent was merged into the $CuSO_4$ solution, a portion of copper sulfate was sorbed by the polymer, eventually reaching an equilibrium with the copper sulfate in the solution. Figure 4-4 shows the percentage $CuSO_4$ sorbed by the polymer relative to the $CuSO_4$ in the original solution. In this system which contains 50.00 ml of copper sulfate solution (copper ion: 1220 ppm or 19.21 mM), the total amount of copper sulfate is 0.96 mmole.

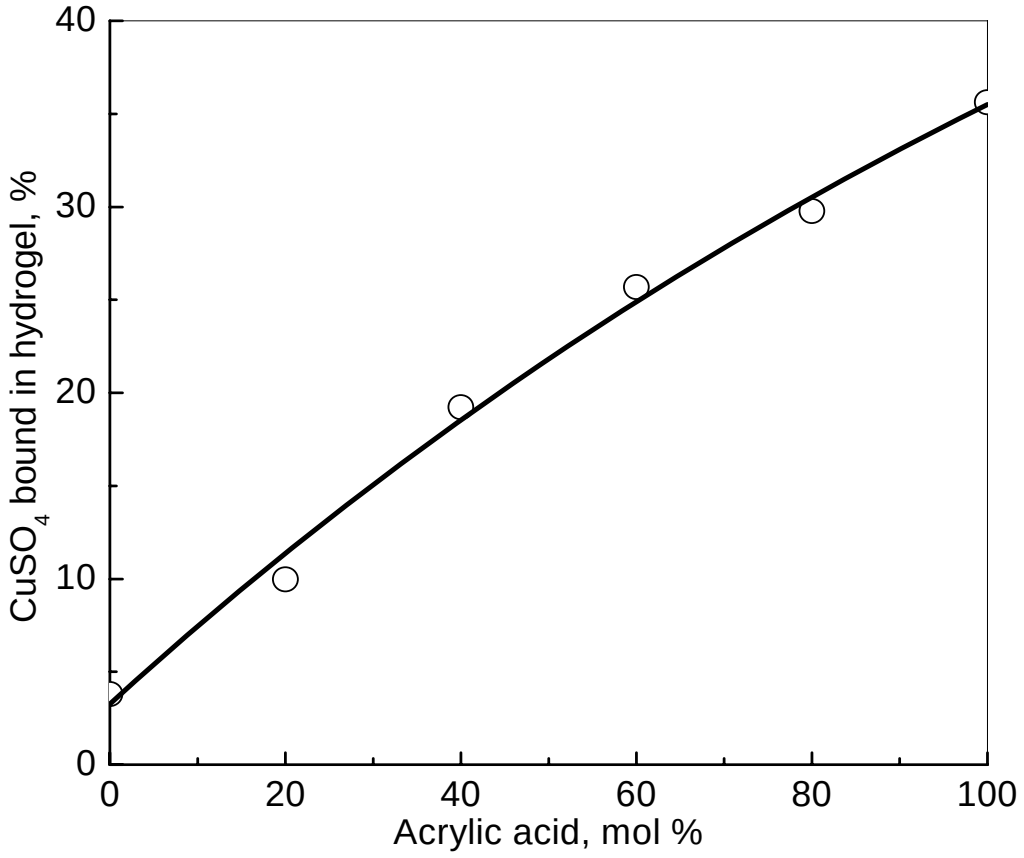

Figure 4- 4 Percentage $CuSO_4$ taken up by the (co)polymers

Experimental conditions are shown in Figure 4-3

It should be pointed out that during the experiment it was found copper ion (II) uptake was accompanied by sodium ion release from the polymers. Sodium ions leave the macromolecular ligands from (-COO^-) and dissipate from the network of the cross-linked copolymers and eventually dissolve into the solution. Figure 4-5 shows the result of sodium ion loss (mmol/g) and copper ion uptake (mmol/g) as a function of the copolymer composition. The ratio of sodium ion loss and copper ion uptake is more than 2, which indicates that copper ion uptake is not a simple ion exchange with sodium ions. Copper ions can form mononuclear and binuclear chelating complexes [Yokoi 1986]. In mononuclear chelating complexes, divalent metal ions can associate with one or two ligands (groups) [Cavus 2009, Barbucci 2002, Rivas 1998B]. Previous work [Yokoi 1986, Cavus 2009, Barbucci 2002, Rivas 1998B] appears to show that one copper ion (II) replace a maximum of two sodium ions. However, the present study indicates that the ratio of sodium ions lost to copper ions gained may exceed 2, depending on polymer composition. For example, at an acrylic acid (sodium acrylate) content of 100, 80 and 60 mol %, the sodium ion loss is 7.73, 6.16 and 5.05 mmol/g, respectively, and the corresponding copper gain is 3.42, 2.86 and 2.47 mmol/g, respectively. The sodium ion loss to copper ion gain ratio appears to be over 2 when acrylic acid (sodium acrylate) is the main component of the copolymer. In an extreme case of poly(acrylic acid) (sodium acrylate), the sodium ion loss to copper ion gain ratio reaches 2.26. This is because 75 % of the acrylic acid in the copolymer has been converted into sodium acrylate during polymer synthesis. A portion of the sodium ions may also dissociate in aqueous solutions. Nevertheless, it seems clear that the copper ion uptake is due to mononuclear chelating

complexation and copper ion sorption is accompanied by sodium ion release from the adsorbent.

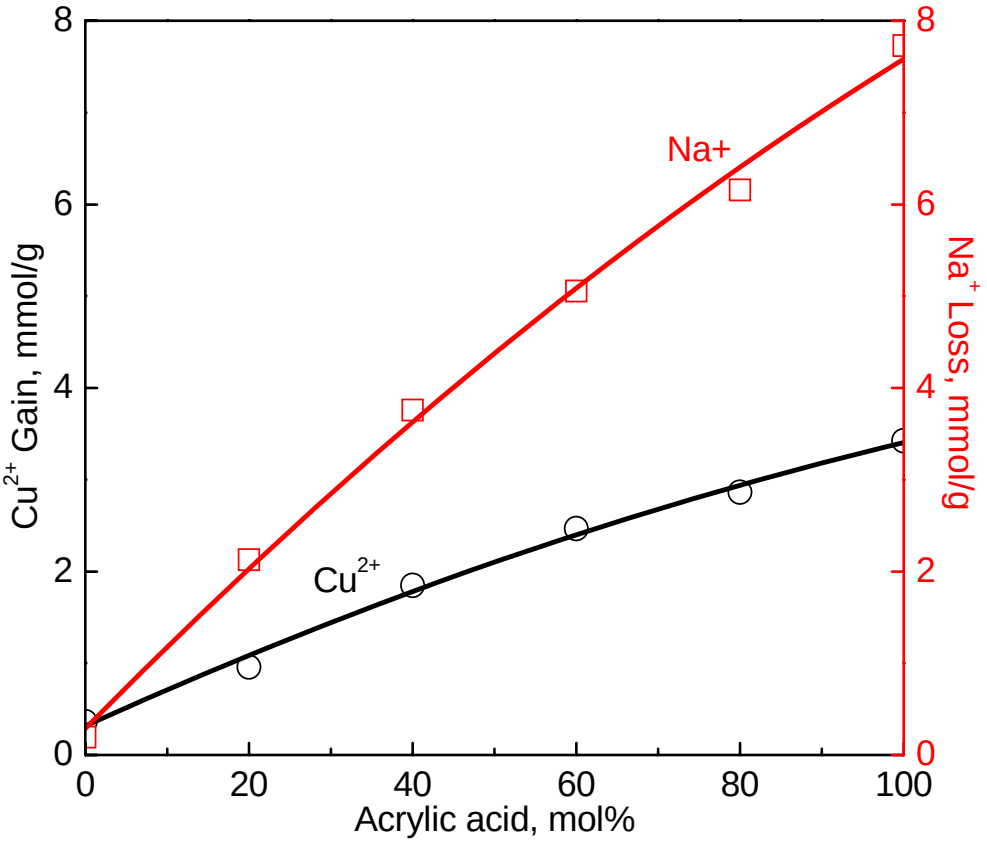

Figure 4- 5 Sodium ion loss and copper ion gain in the copolymers

Experimental conditions are shown in Figure 4-3

4.2.2 Percentage neutralization of carboxyl groups

Many studies have been reported in the literature on the effect of pH on the sorption properties of metal ions in hydrogel materials [Yokoi 1986, Tomida 2001, Li 2002, Cavus 2009, Karakisla 2003, Coskun 2006, Xie 2007, Li 2006, Solener 2008, Atta 2009]. In general, the pH not only determines the state of metal ions in aqueous solutions but also affects the form of the functional carboxyl groups (i.e., –COOH or $-COO^-$). For the copolymer materials, the state of the carboxyl groups determines their sorption behavior. When the carboxyl acid group, –COOH, is neutralized by sodium hydroxide, the acrylic acid will be converted into sodium acrylate, –COONa, which has a high solubility and can exist in an aqueous solution in the form of carboxyl anion, $-COO^-$ and sodium cation, Na^+. In order to study the effect of the state of functional carboxyl groups on water sorption and copper sulfate uptake in the copolymer materials, a portion of the carboxyl acid groups were neutralized so that the copolymers contain both $-COO^-$ and -COOH. The cross-linked copolymers used in these experiments were synthesized using 60 mol % acrylic acid co-monomer (AAc), 40 mol % acrylamide co-monomer (AAm), and 2.0 mol % cross-liking agent (MBA) based on the total quantity of the co-monomers. The carboxyl groups in the AAc chain segments were partially neutralized with sodium hydroxide.

Figure 4-6 shows the effect of percentage acrylic acid neutralized with sodium hydroxide on the copper sulfate uptake and water sorption. The initial quantity of copper sulfate solution was 50.00 ml at an ion concentration of 1550 ppm (24.41mM), the total amount of copper sulfate in the solution was 1.22 mmole. It is shown that both copper sulfate and water sorption increase with an increase in the percentage of acrylic acid

neutralized, i.e. percentage of $-COO^-$ anion in the total number of carboxyl acid groups. The copper sulfate uptake shows a linear relationship with the percentage acrylic acid neutralized. The water uptake, however, increases quickly at low percentage (0-25 mol %) neutralization of acrylic acid and then increases slowly with a further increase in the percentage neutralization from 25 to 100 mol %. These results suggest that the carboxyl acid anion, $-COO^-$, has a higher capacity of binding copper ions and taking up water molecules than carboxyl acid groups, –COOH. The anionic $-COO^-$, an adsorbing active sites [Coskun 2006, Atta 2009, Boonamnuayvitaya 2004, Tahir 2003], is easier to associate with copper ions to form mononuclear and binuclear complexes, favoring the uptake of copper ions. It also has a high sorption capacity for water molecules via hydrogen bond. In addition, according to a previous study [Yokoi 1986], when the carboxyl groups are neutralized with sodium hydroxide, the pH of the aqueous solution depends on the percentage of acrylic acid neutralized. A higher percentage of acrylic acid neutralized will lead to a higher pH, which affects the state of copper ions in aqueous solutions. It has been reported that some copper ions can form inorganic compound $Cu(OH)_2$, which will precipitate and agglomerate at high pH values.

Figure 4-7 shows the percentages of $CuSO_4$ adsorbed by the copolymer versus the percentage neutralization of acrylic acid. The sorption equilibrium was affected by the ratio of the carboxyl acid groups (–COOH) and the carboxyl anion groups ($-COO^-$) in the copolymer. With an increase in the percentage of acrylic acid neutralization, more carboxyl acid groups will be converted to anionic $-COO^-$, and therefore the copper sulfate can easily associate with functional carboxyl groups in the copolymer to form complexes. Consequently, the percentage of $CuSO_4$ sorbed at equilibrium gradually increases.

Compared to the extreme case of 0 neutralization for which 9.7 % of $CuSO_4$ was taken up by the copolymer, when all the –COOH groups were converted to $-COO^-$ anions, the percentage $CuSO_4$ sorbed by the copolymer increased to 24.85 %. This clearly shows that the anionic $-COO^-$ groups have stronger interactions with copper ions than –COOH. In addition, due to the high pH at complete neutralization of acrylic acid by sodium hydroxide, a certain amount of copper sulfate may form $Cu(OH)_2$ in the solution which is not bound to the copolymer sorbent [Yokoi 1986].

Furthermore, Figure 4-8 shows that the sodium ion loss from the copolymer and copper ion gain from the solution are dependent on percentage of acrylic acid neutralized with sodium hydroxide. Both the copper ion gain and sodium ion loss increase with an increase in the percentage neutralization of acrylic acid (pH increases). As expected, if the acrylic acid was not neutralized by sodium hydroxide, copper ions were bound to the copolymer, but there was no sodium lost to the solution. With an increase in the percentage of acrylic acid neutralized, more sodium ions will be released from the copolymer to the solution. The molar ratio of sodium ion loss to copper ion uptake is not always equal to 2. This again suggests that the copper ion uptake is not a simple exchange with sodium ions.

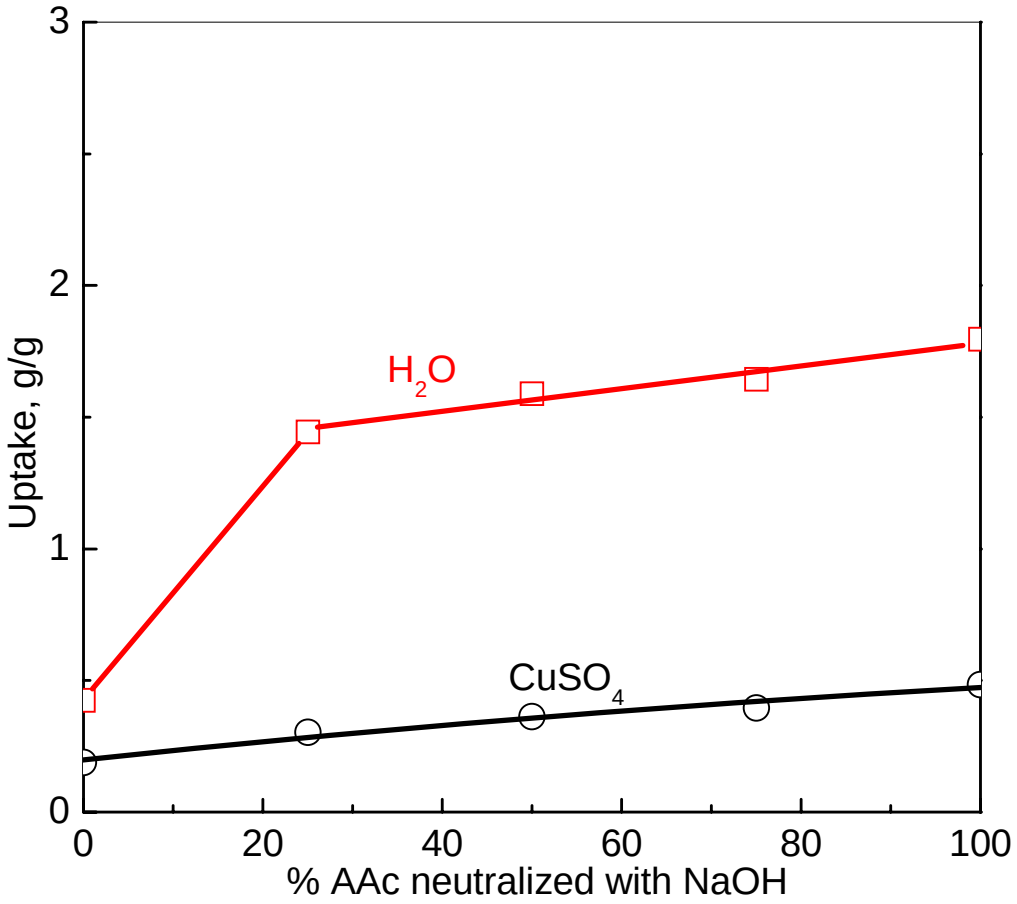

Figure 4- 6 Uptake of $CuSO_4$ and water in copolymers versus percentage of acrylic acid neutralized with sodium hydroxide

The copolymers were synthesized from 60 mol % AAc, 40 mol % AAm and 2 mol % MBA based on total amount of the monomers.

The initial concentration of cooper ion was 1550 ppm (24.41mM).

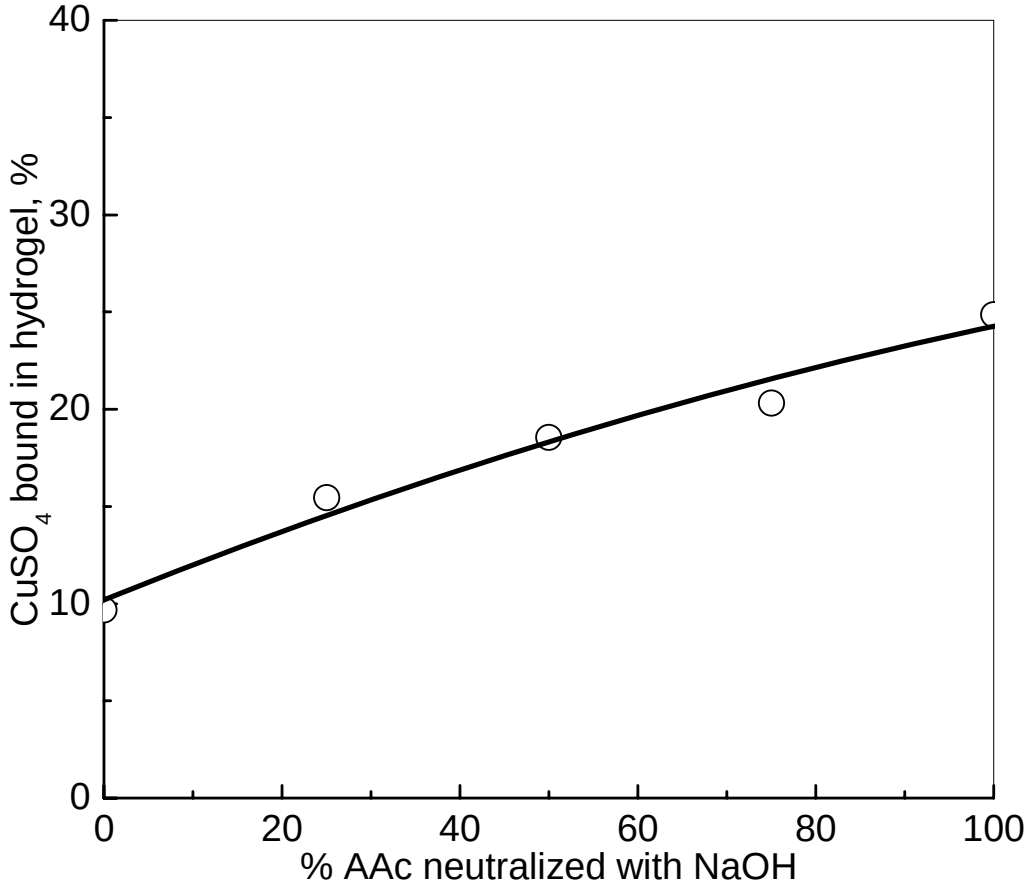

Figure 4- 7 Percentages of $CuSO_4$ taken up by the copolymers at different degree of neutralization of acrylic acid

Conditions of polymer synthesis and sorption test were the same as shown in Figure 4-6.

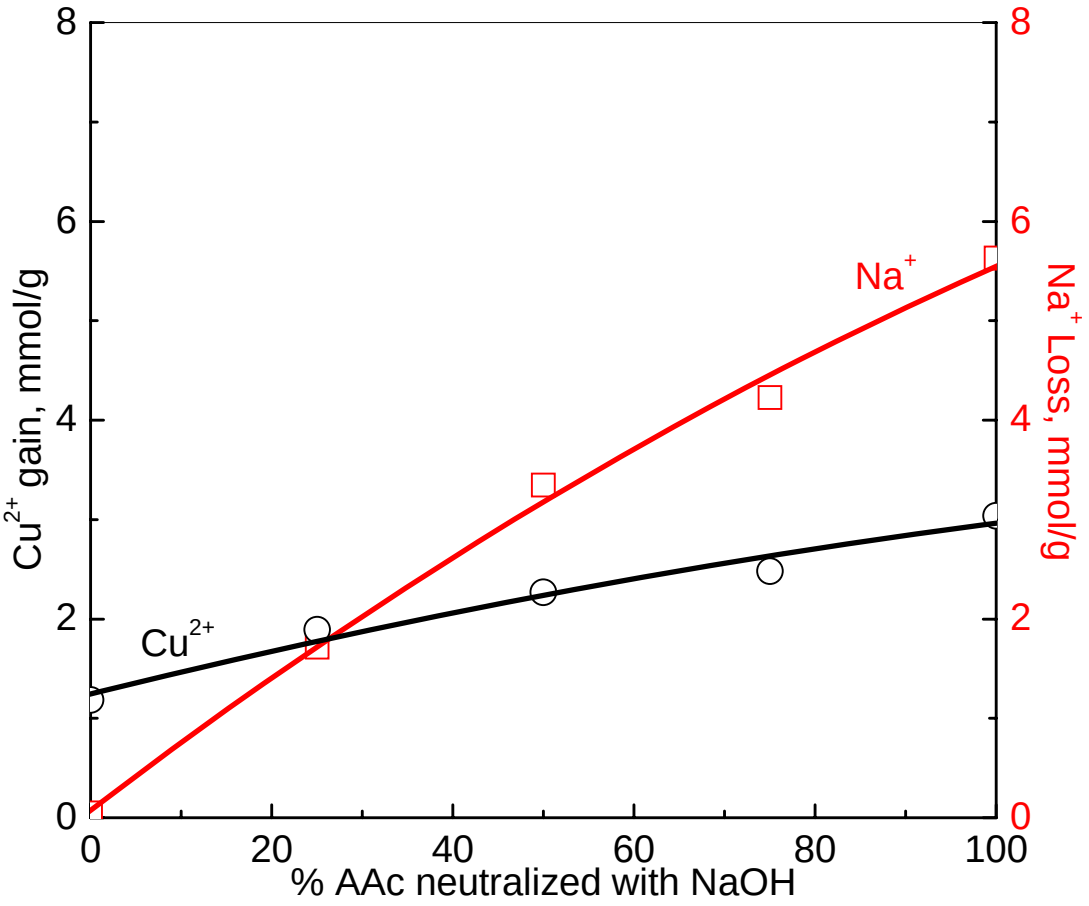

Figure 4- 8 Copper ion gain and sodium ion loss in the sorption process

Conditions of polymer synthesis and sorption test were the same as shown in Figure 4-6.

4.2.3 Degree of cross-linking

The cross-linking of the copolymer will shorten the length of chain segments and reduce the pore size of the cross-linked networks. It can be estimated that as the content of the cross-linking agent in the copolymer increases from 1.0 to 13.8 mol %, the length of chain segments between two cross-linking points will be reduced from 100 to 7.2 units. The copolymers used for this set of experiments comprised of 60 mol % acrylic acid (75 % of carboxyl groups were neutralized with sodium hydroxide) and 40 mol % acrylamide.

Figure 4-9 shows the copper sulfate uptake and water sorption as a function of the content of the cross-linking agent in the copolymers. With an increase in the cross-linking agent content, both the copper sulfate uptake and water sorption decrease, and the decrease in water uptake is more significant, especially at a lower content of the cross-linking agent. As mentioned above, an increase in the degree of cross-linking will shorten the length of chain segments of copolymer network and increase the cross-linking density. As a result, the cross-linked network in the copolymer will have smaller pores, leading to a lower water sorption uptake in the copolymer. On the other hand, the flexibility of the polymer chain affects copper uptake as well. Flexibility is beneficial to the formation of both mononuclear and binuclear complexes [Yokoi 1986]. Increasing the degree of cross-linking will reduce the flexibility of the polymer chain. Therefore, the carboxyl groups in the chain segments will be difficult to associate with copper ions. Consequently, increasing the content of the cross-linking agent in the copolymer will gradually decrease the copper sulfate uptake. In addition, copper sulfate uptake is more mainly influenced by the carboxyl groups in the macromolecular chains than the chain segment length between cross-linking points.

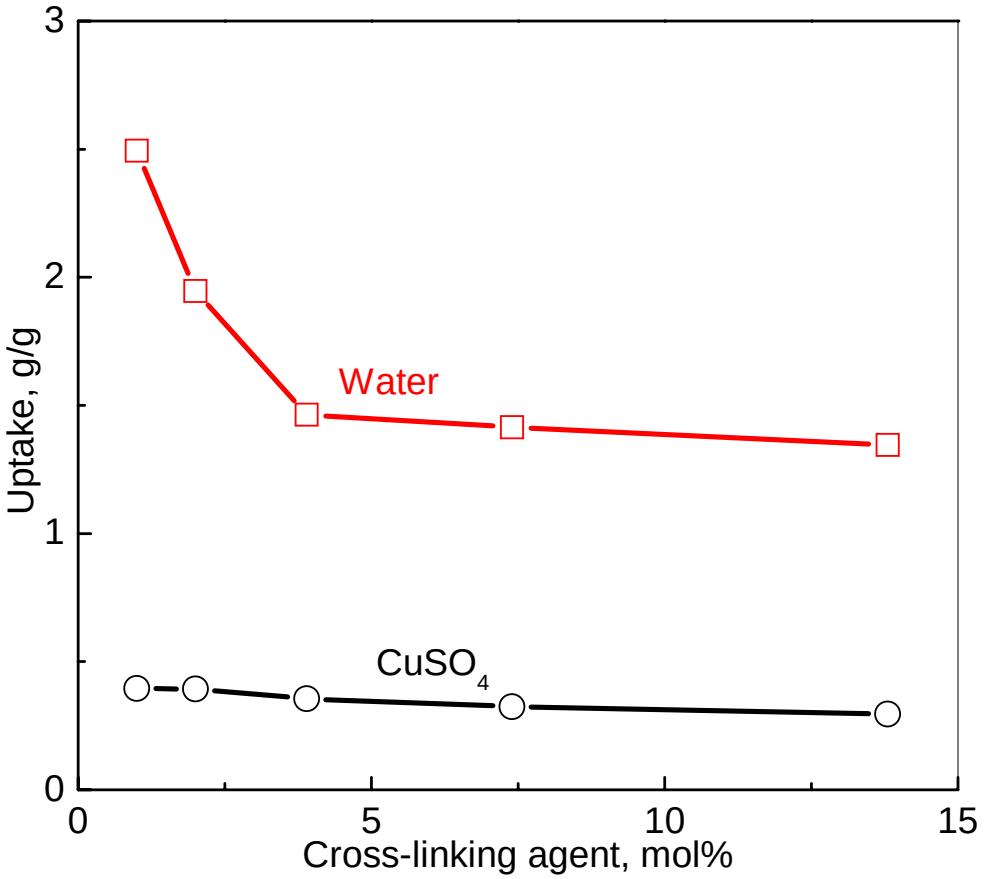

Figure 4- 9 Uptake of $CuSO_4$ and water in copolymers with different content of cross-linking agent.

The copolymers contained 60 mol % AAc (75 % neutralized with sodium hydroxide), and 40 mol % AAm. 50 ml of $CuSO_4$ solution (Cu^{2+}: 1220ppm, 19.21mM) was used in the sorption tests.

The percentage of $CuSO_4$ sorbed by the copolymer is shown in Figure 4-10. Figure 4-11 shows the sodium ion loss and copper ion uptake as a function of the content of the cross-linking agent. Both copper ion uptake and sodium ion loss are shown to decrease with an increase in the content of the cross-linking agent. The molar ratio of sodium ions released and copper ions taken up is slightly greater than 2. When the cross-linking agent increases from 1.0 to 13.8 mol %, the copper ion uptake decreases from 2.5 to 1.8 mmol/g, while the sodium ion released changes from 5.3 to 4.0 mmol/g. These results suggest that the sodium ions released does not seem to result simply from the replacement with copper ions to form chelating complexes. Nevertheless, it can be concluded that the sodium ion release from the copolymer is induced by the copper ion uptake to form mononuclear or binuclear complexes with the functional groups in the copolymer. This agrees with the results of Cavus [2009] and Barbucci [2002].

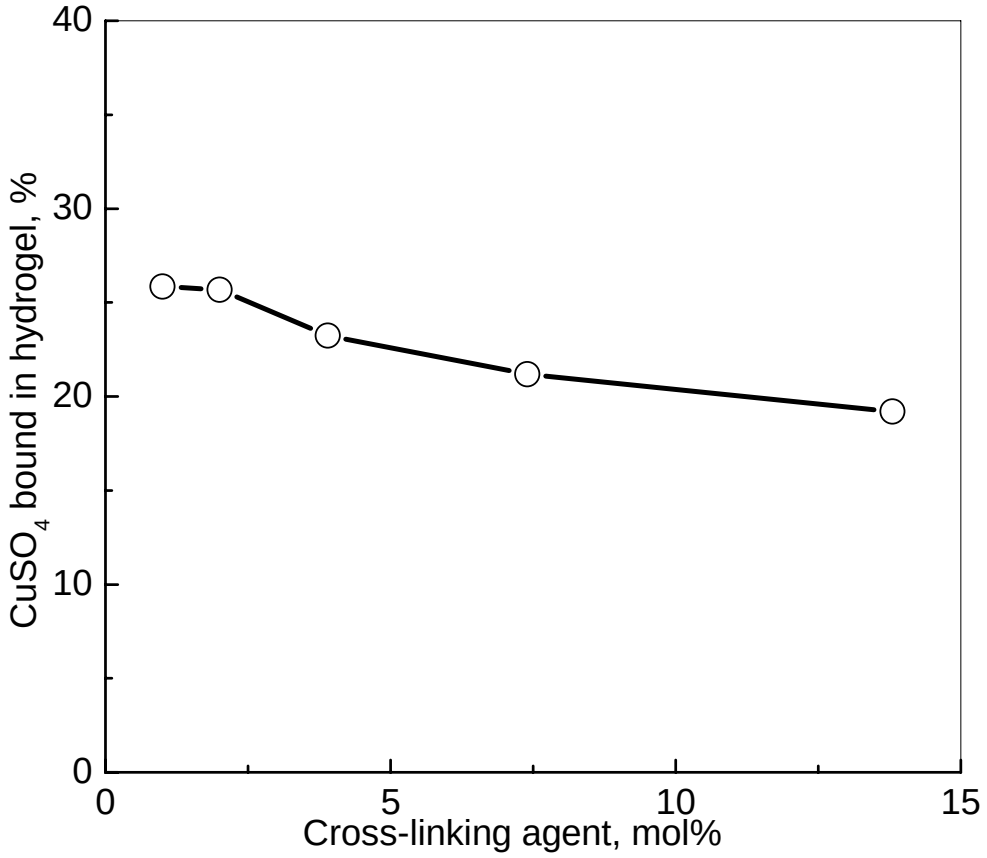

Figure 4- 10 Percentage of $CuSO_4$ sorbed in the copolymers at different degrees of cross-linking

Polymer composition and sorption test conditions are presented in Figure 4-9

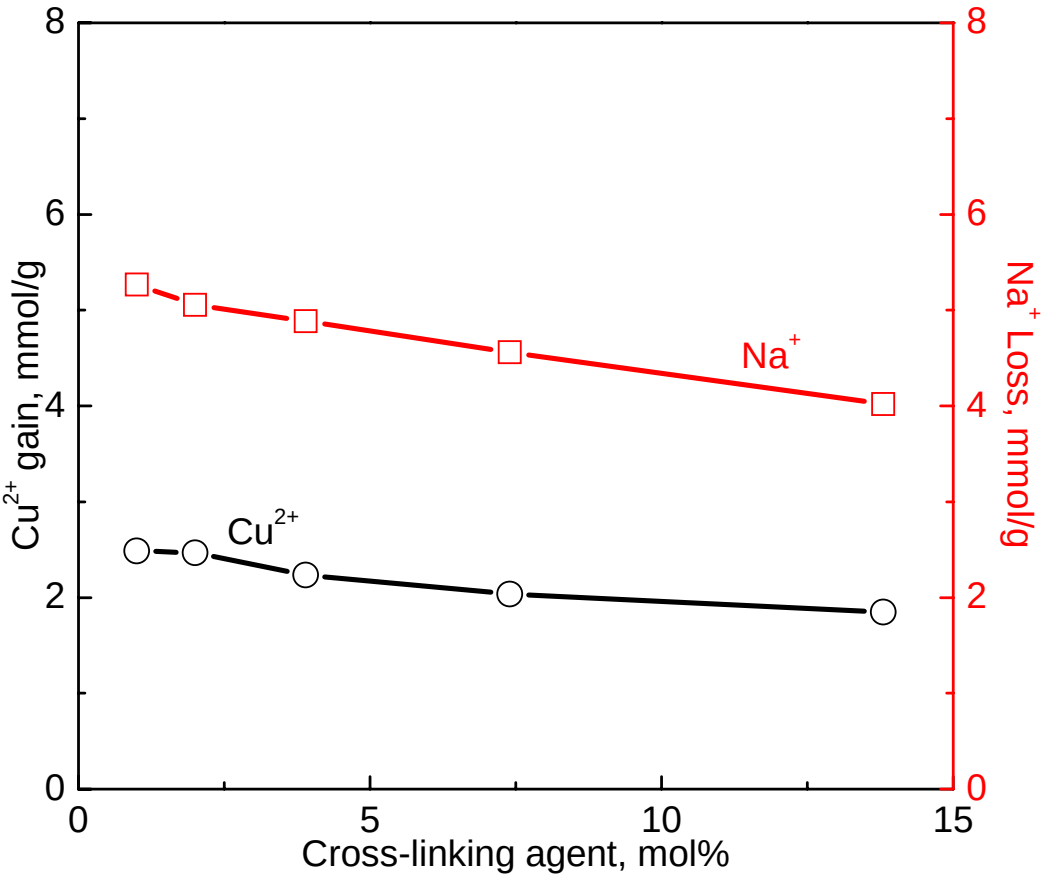

Figure 4- 11 Sodium ions released and copper ions taken up

Polymer composition and sorption test conditions are presented in Figure 4-9

4.3 Sorption isotherm

Figures 4-12 and 4-13 show the sorption uptake of copper sulfate and water as a function of equilibrium concentration of the copper in the sulfate solution, respectively. At a relatively low concentration of copper ion in the solution, the equilibrium sorption uptake of copper sulfate increases drastically with an increase in the copper ion equilibrium concentration in the solution. For example, increasing copper ion equilibrium concentration from 0.03 to 1.34 mM leads to an increase in copper sulfate uptake from 0.005 to 0.37 g/g-polymer. However, when the feed copper concentration is greater than 1.34 mM, a further increase in copper ion concentration does not increase the equilibrium sorption uptake of copper sulfate significantly. This is easy to understand. Because copper sulfate sorption into the copolymer is induced by chelating complexation between copper ions and the active functional groups in the copolymer, the copolymer adsorbent has a strong power to capture the copper ions, even at a low concentration. However, when most of the active functional sites in the sorbent are occupied by copper ions, the copolymer adsorbent will be unable to continue to take additional copper ions effectively, in spite of the higher copper ion concentration in the solution. The strong binding between the copolymer and copper ions will be discussed later in more detail. On the other hand, when copper ions are bound to the copolymer, the water uptake decreases, as expected. This is shown in Figure 4-13. As mentioned previously, copper sorption occurs by chelating complexation, which reduces water uptake due to reduction of the functional groups in the copolymer to sorb water by hydrogel bonding. The copper complexation with the functional groups in the copolymer also acts as cross-linking, making the polymer network more tight and rigid.

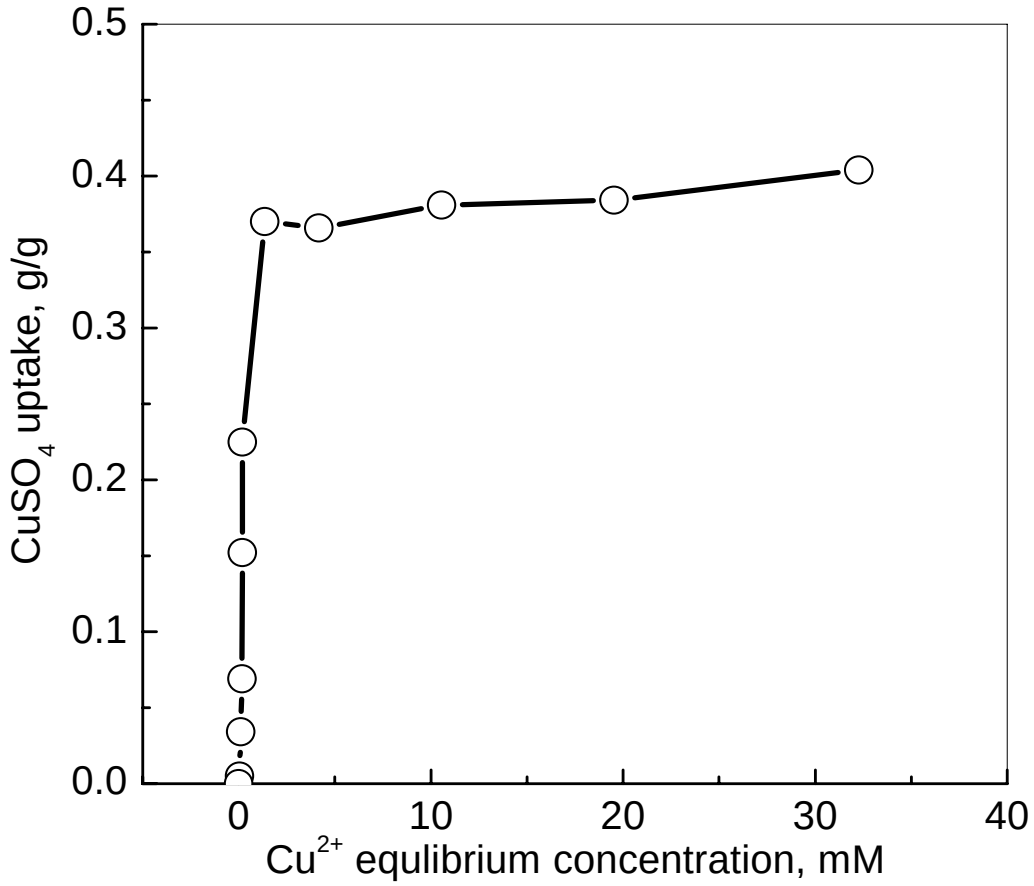

Figure 4- 12 Uptake of $CuSO_4$ in the copolymer as a function of equilibrium concentration in the solution

The copolymer was comprised of 60 mol % AAc (75 % neutralized with sodium hydroxide), 40 mol % AAm, cross-linked with 2 mol % MBA based on the total quantity of the co-monomers.

Based on the data in Figures 4-12 and 4-13, the following physical reasoning can be provided: when the copper ion concentration is relatively low, most of copper ions are bound to form complexes with the carboxyl groups in the copolymer chain. Because of the strong binding power of the copolymer to capture copper ions, its copper ion uptake dramatically increases at this stage. In the meantime, because the carboxyl groups were occupied quickly by copper ions and cannot interact effectively with water molecules by H-bond, the water sorption decreases substantially. For example, the pure water sorption uptake is 179 g/g-polymer. At a copper ion concentration of 1.34 mM in the solution, the equilibrium water uptake is only 1.3 g/g-polymer. In the sorption process, copper ions exchange with sodium ions to directly interact with the functional carboxyl groups in the copolymer chains. Therefore, the more the functional carboxyl groups are occupied to bind copper sulfate, less water will be taken up by the copolymer.

Figure 4-14 shows the copper ion uptake and sodium ion release as a function of equilibrium concentration of copper ion in the solution. At low concentrations, the molar quantity of sodium ion release is more than two times of copper ion uptake. This is because in addition to exchange between copper ions and sodium ions (which gives a molar ratio of sodium release to copper uptake of 2 based on stoichiometry), some sodium ions in the copolymer dissociate and enter the solution phase. However, at relatively high copper concentrations in the solution, the copper ions will not only complex with the hydroxyl groups but also interact with the amide groups, resulting in a sodium release to copper uptake ratio of slightly lower than 2.

Based on the above analysis, it can be seen that at sorption equilibrium, all copper ions, water and sodium ions will reach equilibrium between the solution phase and the

polymer phase. The sorption uptake of copper influences the equilibrium of sodium and water between the solution phase and polymer phase significantly.

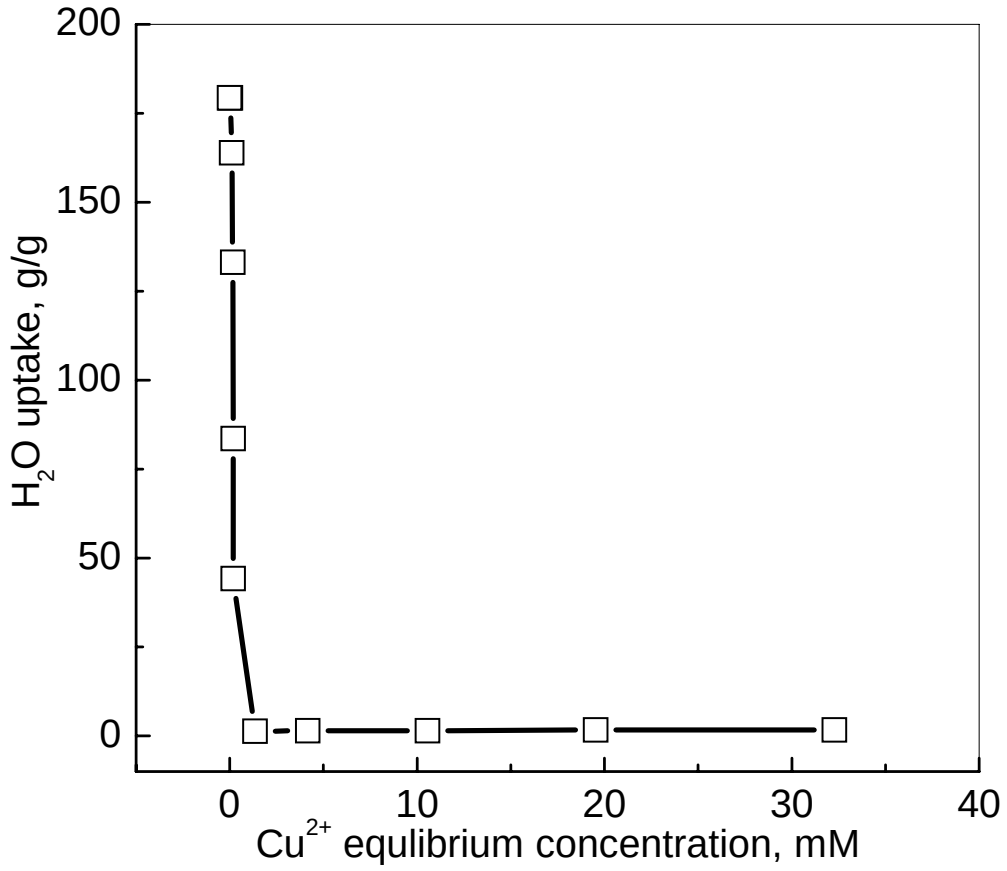

Figure 4- 13 Sorption uptake of water in the copolymer as a function of equilibrium concentration of copper in the solution

Polymer composition was the same as shown in Figure 4-12

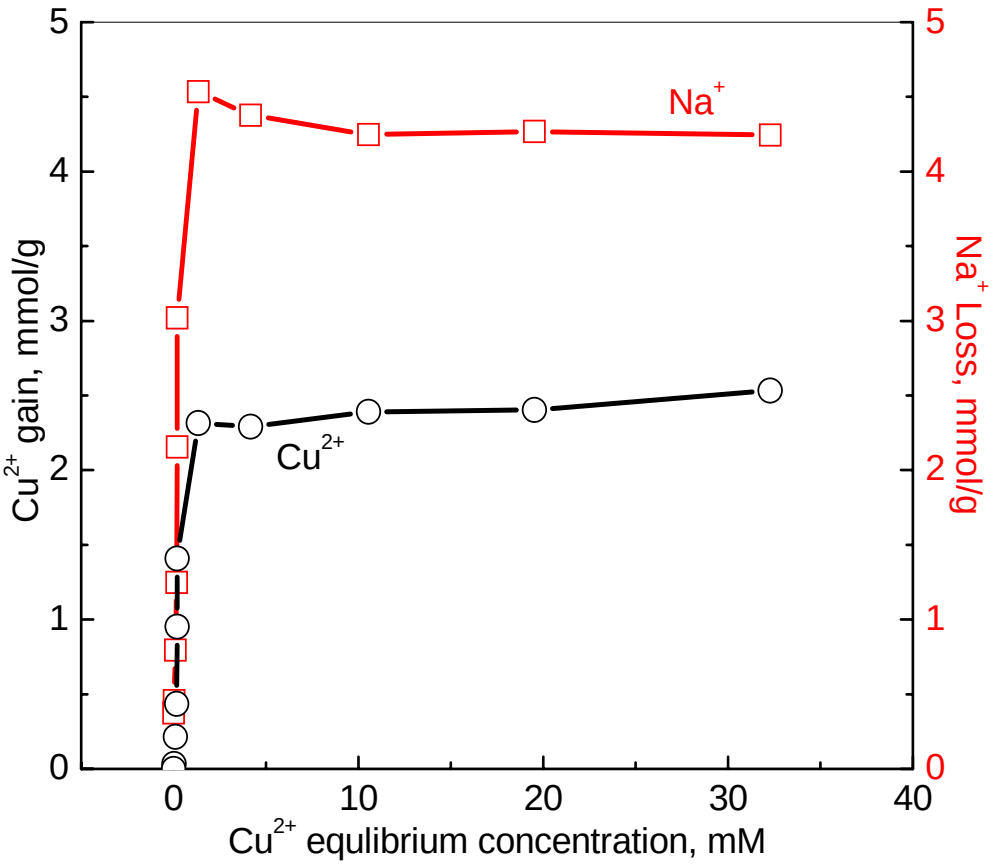

Figure 4- 14 A comparison of copper ion uptake and sodium ion release as a function of equilibrium concentration of copper in the solution

Polymer composition was the same as shown in Figure 4-12

The sorption isotherm data were analyzed with Langmuir equation and Freundlich equation. The Langmuir model is based on monolayer adsorption on the active sites of an adsorbent, representing chemisorption on a set of distinct localized adsorption sites. It

assumes that the forces between sorbed molecules are negligible, and once a molecule occupies a site no further sorption take place. Figure 4-15 shows that the sorption data at low concentration range (<10 mM) can be represented by the Langmuir isotherm equation with a correlation coefficient (R^2) of 0.972. It should be pointed out that the active sorptive sites, carboxyl groups, associate with copper ions to form chelating complexes with one or two ligands [Rivas 1998B, Cavus 2009]. The functional carboxyl groups in the chain segments of the copolymer network can not move freely toward copper ions to form complexes because the flexibility of chain segments of the copolymer declines once sorption occurs. Based on Langmuir isotherm, the maximum sorption capacity in the copolymer (q_{max}) is 2.58 mM/g and the binding constant (K_L) is 2.9 l/mM.

The Freundlich isotherm model was also tested to fit the experimental data. Unfortunately, it was found that the Freundlich model did not work for the sorption system studied here. In principle, the Freundlich model should work well for multi-layer sorption systems. Because copper sorption occurs via chelating complexation, once a hydroxyl site is occupied by a copper ion, it will be difficult to interact with additional cooper ions. It is not surprising that the Langmuir model works better than the Freundlich model to describe the copper sorption in the copolymer sorbent.

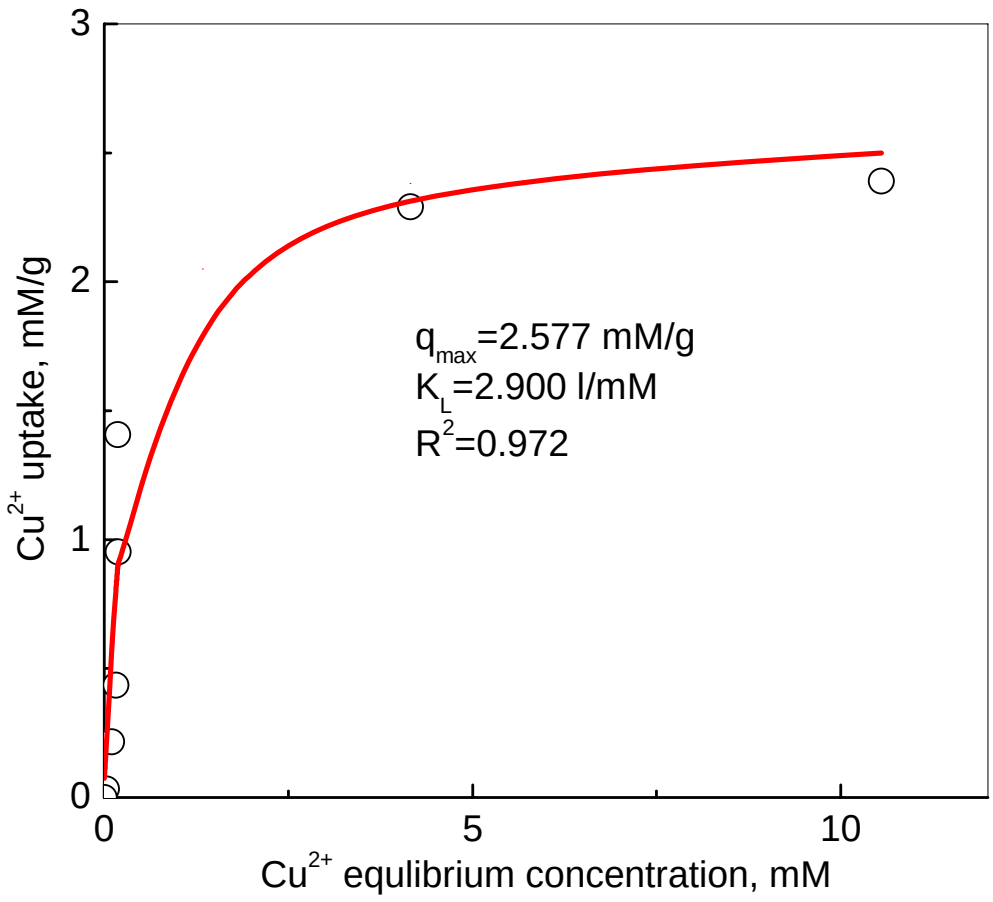

Figure 4- 15 Sorption isotherm of copper as represented by the Langmuir isothermal model

4.4 Qualitative observation on copper adsorption

At first, the dried copolymer sample was immersed into deionized water for three days to become fully saturated, and then the hydrogel sample was taken out and weighed.

The soft and wet hydrogel sample, which was transparent, then was immersed in 500ml copper sulfate solution at 94 ppm for 3 days to reach sorption equilibrium. It was found that the copolymer sample shrank in size after sorbing copper sulfate, and some water in the hydrogel was released. The hydrogel containing copper sulfate became light blue in color.

When the hydrogel sample was transferred into another copper sulfate solution at a higher concentration (174 ppm), the blue spot coverage increased and a darker blue layer was observed on the outer surface of the hydrogel sample. However, the inner part of the hydrogel sample was still transparent. It appeared that the copper–carboxyl complexes acted as barrier which restricted the diffusion of copper ions from the solution to the interior of the hydrogel. Further increasing copper sulfate solution concentration (from 382 to 1396 ppm), the blue outer layer became thicker and the sample shrank further to form a more rigid and less swollen solid. This is shown in Figure 4-16, and the weight change of the sample was shown in Table 4-1.the weight loss is due to the water molecules coming out form the copolymer hydrogel.

When the copolymer adsorbs water, the network pores of the cross-linked copolymer retains a large amount of water molecules due to strong interaction between water molecules and the hydrophilic carboxyl groups in the macromolecular chain. When copper ions are bound to the copolymer by chelating complexation, the water molecules can no longer be retained, and the hydrogel will begin to lose water, causing shrinkage in the copolymer sample. The copper sorption and the accompanied water loss are clearly demonstrated here. Figure 4-17 is a scheme illustrating water loss from the hydrogel caused by copper sorption into the copolymer. As shown in this Figure, some water

molecules interact with carboxyl groups on macromolecular chain by H-bonding. The other water molecules are held in hydrogel by interaction such as H-bonding, Van de Waals force. When copper ions enter the pore of hydrogel and associate with carboxyl groups, all the water molecules were excluded from the pore and copper ions complexes were formed. Base on the Figure, it is easier for carboxyl anions to associate with copper cations than carboxyl acid.

Table 4- 1 Weight of the hydrogel in copper sulfate solutions at different concentrations

	A	**B**	**C**	**D**	**E**	**F**
Concentration of $CuSO_4$, ppm	0	94	174	382	736	1396
Weight, g	113.0	88.0	2.608	1.276	0.858	0.819

The chelating complexes acted as an internal cross linking, which provided a barrier for copper ions in the liquid solution to penetrate the copolymer, resulting in a “core-and shell” structure where the core is difficult to reach by copper ions in the solution. This was why in previous sorption studies all the copolymer samples were ground to fine powders to ensure the sorption took place uniformly.

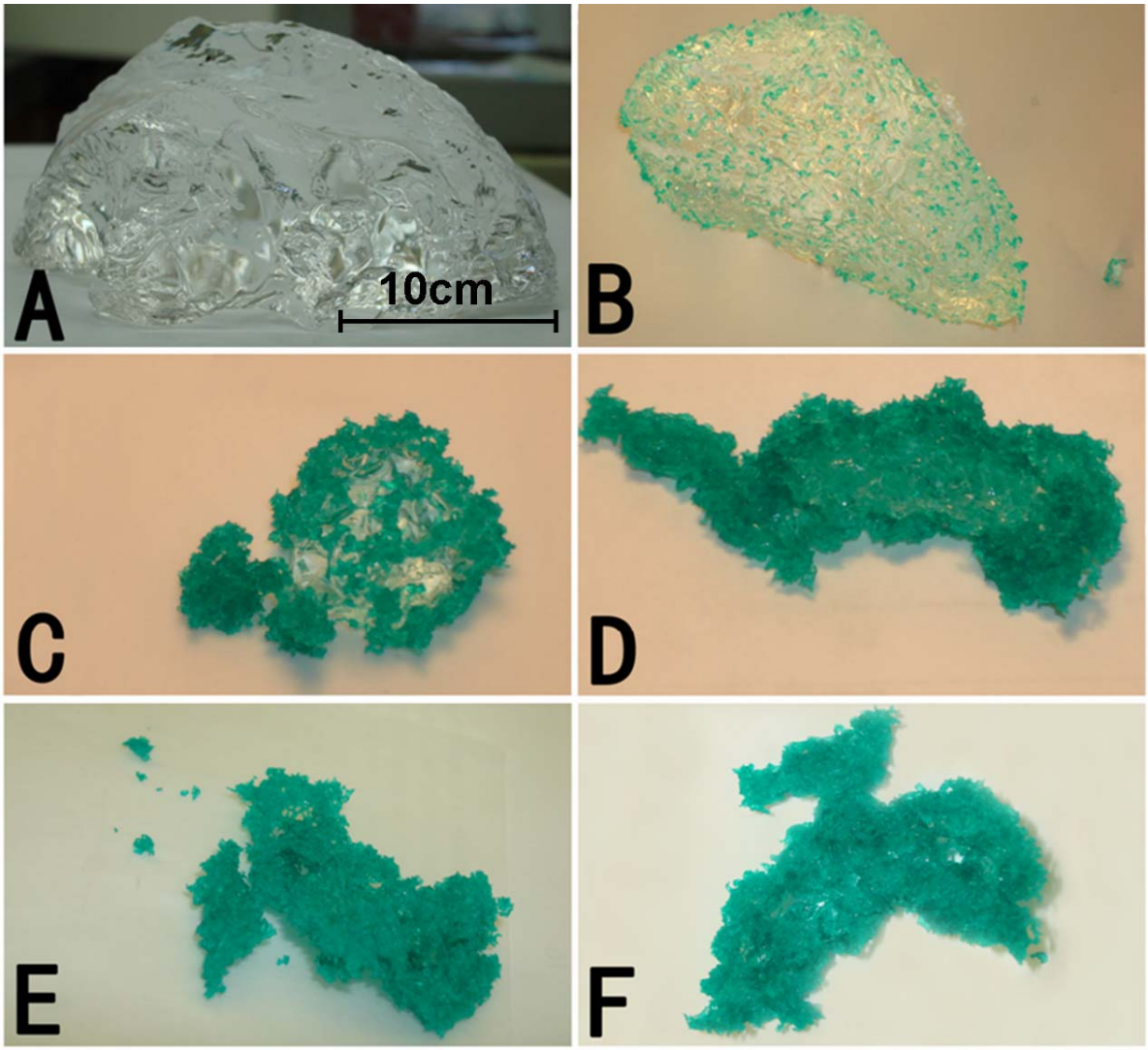

Figure 4- 16 A: hydrogel swollen in pure water; B: in copper sulfate solution at 94 ppm (1.48mM); C: 174 ppm (2.74mM); D: 382 ppm (6.01mM); E: 736 ppm (11.59mM); F: 1396 ppm (21.98mM)

The copolymer composition: 60 mol % AAc (75 % neutralized with sodium hydroxide) and 40 mol % AAm, cross-linked with 2 mol % MBA based on total amount of co-monomers.

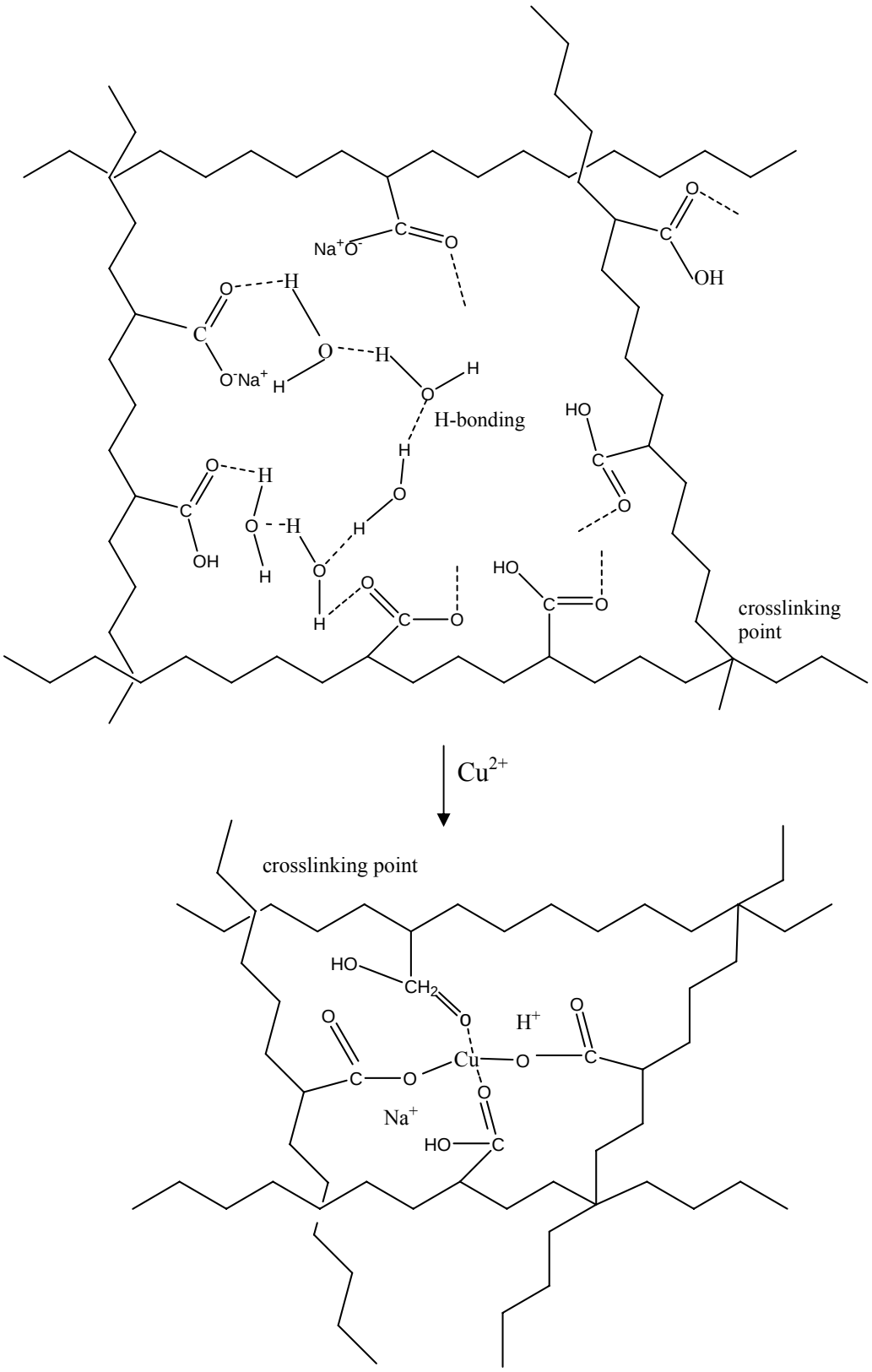

Figure 4- 17 Process of hydrogel losing water molecules

4.5 WAXD spectrum of the copolymer containing $CuSO_4$

Copper sulfate is a crystalline inorganic compound. When bound to the copolymer, the crystalline structure will disappear because copper ions form chelating complexes with the carboxyl groups. This has been confirmed by the wide angle X-ray diffraction (WAXD).

Figure 4-18 shows the WAXD spectrum of pure $CuSO_4$ sample and the dried copolymer containing $CuSO_4$. The sharp peaks in the spectrum of pure $CuSO_4$ indicate its crystalline structure. No peaks were visible in the WAXD spectrum of the dried hydrogel sample containing $CuSO_4$ sorbate. This result suggests that the copper sulfate sorbed in the hydrogel is in a non-crystalline form, which is consistent with the above explanation that copper ions form complexes with the hydroxyl groups in the copolymer. The carboxyl groups in the acrylic acid chain segments are easy to associate with copper ions [Yoon 2005] and copper sulfate does not aggregate in the hydrogel as an isolated dispersed phase but associates with the ligands to form complexes.

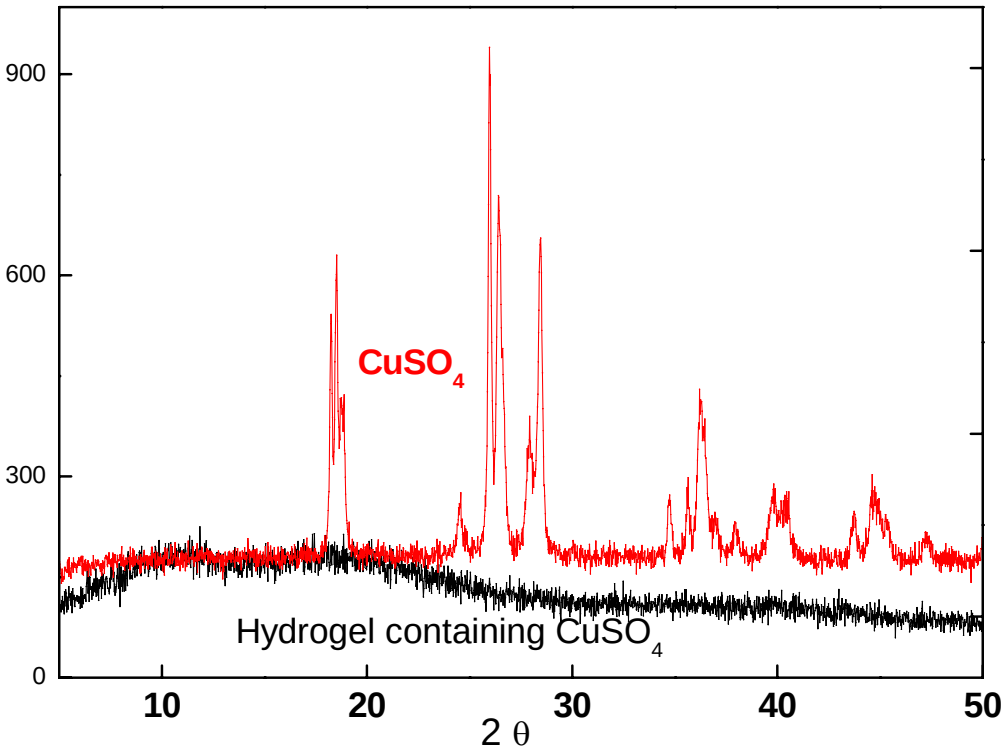

Figure 4- 18 WAXD spectrum of $CuSO_4$ and the copolymer hydrogel containing $CuSO_4$

The copolymer composition: 60 mol % AAc (75 % neutralized with sodium hydroxide) and 40 mol % AAm, cross-linked with 2 mol % MBA based on total amount of co-monomers.

CHAPTER 5 GENERAL CONCLUSIONS AND RECOMMENDATIONS

5.1 General conclusions

Copolymers of acrylic acid and acrylamide were synthesized by free radical polymerization in aqueous solutions. The copolymers were comprised of different contents of acrylic acid (where the carboxyl groups were partially neutralized by sodium hydroxide) and were cross-linked with different amounts of MBA. These copolymers were tested for copper sorption for aqueous solutions. The following conclusions can be drawn from this research:

(1) The effect of macromolecular structure on water sorption and metal ion (Cu^{2+}) uptake is systematically investigated.

(2) With an increase in the content of the acrylic acid (sodium acrylate), copper sulfate uptake increases, and water sorption decreases quickly and then gradually increases when the acrylic acid content is high enough. Copper ion uptake is accompanied with a release of sodium ions from the copolymer.

(3) Increasing the percentage of the carboxyl groups neutralized by sodium hydroxide will increase the uptake of copper sulfate and water. Copper ion uptake is a major factor for sodium ion loss from the copolymer.

(4) With an increase in the content of the cross-linking agent, both copper sulfate uptake and water sorption decrease.

(5) At relatively low concentrations of $CuSO_4$ in water, the copper sulfate sorption into the copolymer follows the Langmuir model.

(6) When copper ions replace sodium ions to interact with carboxyl groups in the copolymer to form chelating complexes, the water sorption decreases substantially.

5.2 Recommendations

The following are recommendations for future investigation:

(1) Hydrogels are soft materials with many special properties. Their applications can be expanded. For example, the copolymers of acrylic acid and acrylamide may be used to separate water from organic compounds because of their excellent hydrophilicity.

(2) The mechanism of metal sorption into the copolymer and details about the chelating complexation need further studies.

(3) The polymer synthesis conditions (e.g. co-monomer composition, temperature, cross-linking agent) may be optimized for given applications.

REFERENCES

Akkaya, R. and U. Ulusoy, Adsorptive features of chitosan entrapped in polyacrylamide hydrogel for Pb^{2+}, UO_2^{2+}, and Th^{4+}, *Journal of Hazardous Materials*, 2008, Vol 151: 380–388.

Ali, E-H A., H.A. Shawky, H.A.E.A. Rehim and E.A. Hegazy, Synthesis and characterization of PVP/AAc copolymer hydrogel and its applications in the removal of heavy metals from aqueous solution. *European Polymer Journal*, 2003, Vol 39(12): 2337-2344.

Atta, A.M., E.M. Abdel-Bary, K. Rezk and A. Abdel-Azim, Fast responsive poly(acrylic acid-co-N-isopropyl acrylamide) hydrogels based on new crosslinker, *Journal of Applied Polymer Science,* 2009, Vol 112: 114–122.

Bailey, S.E., T.J. Olin, R.M. Bricka and D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Research*, 1999, Vol 33(11): 2469-2479.

Barbucci, R., G. Leone, A. Magnani, L. Montanaro, C.R. Arciola, G. Peluso and O. Petillo, Cu^{2+} and Ag^{+}-complexes with a hyaluronane-based hydrogel, *Journal of Materials Chemistry*, 2002, Vol 12: 3084–3092.

Benegas, J.C., R.F.M.J. Cleven and M. A.G.T. van den Hoop, Potentiometric titration of poly(acrylic acid) in mixed counterion systems: Chemical binding of Cd ions, *Analytica Chimica Acta*, 1998, Vol 369: 109-114.

Bjerrum, J., "Metal Ammine Formation in Aqueous Solution," P. Haase, Copenhagen, 1941.

Boonamnuayvitaya, V., C. Chaiya, W. Tanthapanichakoon and S. Jarudilokkul, Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay, *Separation and Purification Technology*, 2004, Vol 35: 11–22.

Campbell, D., L.K. Monteith and T.J. Turner, Post-irradiation free-radical reactions in poly (ethylene terephthalate), *Journal of Polymer Science: Part A-1*, 1970, Vol 8(9): 2703-2711.

Cavus, S., G. Gurdag, K. Sozgen and M.A. Gurkaynak, The preparation and characterization of poly(acrylic acid-co-methacrylamide) gel and its use in the non-competitive heavy metal removal, *Polymers for Advanced Technologies*, 2009, Vol 20(3): 165-172.

Coskun, R., C. Soykan and M. Sacak, Adsorption of copper(II), nickel(II) and cobalt(II) ions from aqueous solution by methacrylic acid/acrylamide monomer mixture grafted poly(ethylene terephthalate) fiber, *Separation and Purification Technology*, 2006, Vol 49: 107–114.

Do, D.D., Adsorption analysis: Equilibia and kinetics, Imperial College Press, 1998, Daners, Massachusetts.

Endo, N., H. Shirota and K. Horie, Deuterium Isotope effect on the phase separation of zipper-type hydrogen-bonding inter-polymer complexes in solution, *Macromolecular Rapid Communication*, 2001, Vol 22: 593-597.

Esser-Kahn, A.P., A.T. Lavarone and M.B. Francis, Metallothionein-cross-linked hydrogels for the selective removal of heavy metals from water, *Journal of the American Chemical Society*, 2008, Vol 130 (47): 15820-15822.

Esser-Kahn, A.P. and M.B. Francis, Protein-cross-linked polymeric materials through site-selective bioconjugation, *Angewandte Chemie International Edition*, 2008, Vol 47(20): 3751 –3754.

European Commission, Heavy metals in waste final report, 2002, Denmark. http://www.pb-free.com/pdf/weee-rohs_info/heavymetals.pdf

Gilmore, J.M., R.A. Scheck, A.P. Esser-Kahn, N.S. Joshi and M.B. Francis, N-terminal protein modification through a biomimetic transamination reaction, *Angewandte Chemie International Edition,* 2006, Vol 45(32): 5307 –5311.

Gregor, H.P., L.B. Luttinger and E.M. Loebl, Metal-polyelectrolyte complexes I. The polyacrylic acid-copper complex*, Journal of Physical Chemistry*, 1955, Vol 59(1): 34-39.

Ho, Y.S., D.A.J. Wase, and C.F. Forster, Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat, *Environmental Technology,* 1996, Vol 17(1): 71-77.

Huang, F., Y. Zheng and Y. Yang, Study on macromolecular metal complexes: synthesis, characterization, and fluorescence properties of stoichiometric complexes for rare Earth Coordinated with Poly(acrylic acid), *Journal of Applied Polymer Science,* 2007, Vol 103: 351–357 .

Humphrey, J.L. and G.E. Keller, Separation Process Technology, McGraw-Hill, 1997, New York.

Ilmain, F., T. Tanaka and E. Kokufuta, Volume transition in a gel driven by hydrogen bonding, *Nature*, 1991, Vol 349: 400.

Isogai, N., T. Narita, L. Chen, M. Hirata, J.P. Gong and Y. Osada, Polymer–surfactant interactions: their co-operativity and Stoichiometry, *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*, 1999, Vol 147: 189–201.

Karakisla, M., The adsorption of Cu(ii) ion from aqueous solution upon acrylic acid grafted poly(ethylene terephthalate) fibers, *Journal of Applied Polymer Science,* 2003, Vol 87: 1216–1220.

Kasgoz, H., S. Ozgumus and M Orbay, Preparation of modified polyacrylamide hydrogels and application in removal of Cu(2) ion, *Polymer*, 2001, Vol 42: 7497-7502.

Kasgoz, H., S. Ozgumus and M. Orbay, Modified polyacrylamide hydrogels and their application in removal of heavy metal ions, *Polymer*, 2003, Vol 44: 1785-1793.

Katono, H., A. Maruyama, K. Sanui, N. Ogata, T. Kano and Y. Sakurai, Thermo-responsive swelling and drug release switching of interpenetrating polymer networks composed of poly (acrylamide-co-butyl methacrylate) and poly (acrylic acid), *Journal of Controlled Release,* 1991, Vol 16: 215-228.

Kawaguchi, H., Functional polymer microspheres, *Progress in polymer Science*, 2000, Vol 25: 1171-1210.

Lester, J.N., Heavy metals in wastewater and sludge treatment process, Volume I, Sources, analysis, and legislation, CRC Press, 1987, Boca Raton, Florida.

Li, N. and R. Bai, Highly enhanced adsorption of lead ions on chitosan granules functionalized with poly(acrylic acid), *Industrial & Engineering Chemistry Research,* 2006, Vol 45: 7897-7904.

Li, W., H. Zhao, P.R. Teasdale, R. John and S Zhang, Synthesis and characterisation of a polyacrylamide–polyacrylic acid copolymer hydrogel for environmental analysis of Cu and Cd, *Reactive & Functional Polymers*, 2002, Vol 52: 31–41.

Masaaki, I., The pH of weak polyacid solutions in the presence of mono- and divalent counterions, *Macromolecules*, 1979, Vol 12(3): 498.

Masri, M.S., F.W. Reuter and M. Friedman, Binding of metal cations by natural substances, *Journal of Applied Polymer Science,* 1974, Vol 18: 675-481.

McKay, G., H.S. Blair and A. Findon, Equilibrium studies for the sorption of metal ions onto chitosan, *Indian Journal of Chemistry, Part A*, 1989, Vol 28: 356-360.

Nguyen, K.T. and J.L. West, Photopolymerizable hydrogels for tissue engineering applications, *Biomaterials*, 2002, Vol 23: 4307–4314.

Okuzaki, H. and Y. Osada, Role and effect of cross-linkage on the polyelectrolyte-surfactant interactions, *Macromolecules*, 1995, Vol 28: 4554-4557.

Osada, Y., H. Okuzaki and H. Hori, A polymer gel with electrically driven motility, *Nature*, 1992, Vol 355: 242.

Osada. Y. and J.P. Gong, Soft and wet materials: polymer gels, *Advanced Materials*, 1998, Vol 10(11): 827-837.

Porasso, R.D., J.C. Benegas, and A.G.T. van den Hoop Marc, Chemical and electrostatic association of various metal ions by poly(acrylic acid) and poly(methacrylic acid) as studied by potentiometry, the *Journal of Physical Chemistry. B,* 1999, Vol 103(13): 2361-2365.

Porasso, R.D., J.C. Benegas, A.G.T. van den Hoop M and S. Paoletti, Analysis of potentiometric titrations of heterogeneous natural polyelectrolytes in terms of

counterion condensation theory: application to humic acid, *Biophysical Chemistry*, 2000, Vol 86: 59-69.

Rivas, B.L., B. Quilodran and E Quiroz, Metal ion retention properties of poly(acrylic acid) and poly[*n*-3-(dimethylamino)propyl acrylamide-*co*-acrylic acid], *Journal of Applied Polymer Science*, 2005, Vol 97: 1385–1394.

Rivas, B.L. and G.V. Seguel, Polychelates of poly(acrylic acid-*co*-acrylamide) with Cu(II), Co(II), and Ni(II), *Polymer Bulletin*, 1998, Vol 40: 431–437.

Rivas, B. L., S.A. Pooley, M. Soto, H.A. Maturana and K.E. Geckeler, Poly (N,N*-dimethylacrylamide-co-acrylic acid): synthesis, characterization, and application for the removal and separation of inorganic ions in aqueous solution, *Journal of Applied Polymer Science*, 1998, Vol. 67: 93–100.

Rivas, B.L. and S. Villegas, Water-insoluble polymers with ability to remove metal ions, *Journal of Applied Polymer Science*, 2004, Vol. 91, 3679–3685.

Sag, Y. and Y. Aktay, Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and Rhizopus arrhizus, *Biochemical Engineering Journal*, 2002, Vol 12: 143–153.

Schwarzenbach, R.P., B.I. Escher, K. Fenner,, T.B. Hofstetter, C.A. Johnson, U. von Gunten and B. Wehrli, The challenge of micropollutants in aquatic systems, *Science,* 2006, Vol 313: 1072–1077.

Shibi, I.G. and T.S. Anirudhan, Synthesis, characterization, and application as a mercury (ii) sorbent of banana stalk (solener paradisiaca)-polyacrylamide grafted copolymer bearing carboxyl groups, *Industrial & Engineering Chemistry Research,* 2002, Vol 41: 5341-5352.

Shibi, I.G. and T.S. Anirudhan, Adsorption of Co(II) by a carboxylate-functionalized polyacrylamide grafted lignocellulosics, *Chemosphere*, 2005, Vol 58: 1117–1126.

Solener, M., S. Tunali, A.S. Ozcan, A. Ozcan and T. Gedikbey, Adsorption characteristics of lead(II) ions onto the clay/poly(methoxyethyl)acrylamide (PMEA) composite from aqueous solutions, *Desalination*, 2008, Vol 223: 308–322.

Tanaka, T., I. Nishio, S.T. Sun and S. Ueno-Nishio, Collapse of gels in an electric field, *Science,* 1982, Vol 218: 467.

Tahir, S.S. and N. Rauf, Thermodynamic studies of Ni(II) adsorption onto bentonite from aqueous solution, T*he Journal of Chemical Thermodynamics*, 2003, Vol 35: 2003–2009.

Tomida, T., K. Hamaguchi, S. Tunashima, M. Katoh and S. Masuda, Binding properties of a water-soluble chelating polymer with divalent metal ions measured by ultrafiltration. poly(acrylic acid), *Industrial & Engineering Chemistry Research*, 2001, Vol 40: 3557-3562.

Tsutsui, H., M. Moriyama, D. Nakayama, R. Ishii and R. Akashi, Synthesis and temperature-responsive properties of novel semi-interpenetrating polymer networks consisting of a poly(acrylamide) polymer network and linear poly(acrylic acid) chains, *Macromolecules,* 2006, Vol *39:* 2291-2297.

Xie, J., X. Liu and J. Liang, Absorbency and adsorption of poly(acrylic acid-co acrylamide) hydrogel, *Journal of Applied Polymer Science*, 2007, Vol 106: 1606–1613.

Woessner, D.E. and B.S. Snowden, Pulsed NMR study of water in agar gels, *Journal of Colloid and Interface Science,* 1970, Vol 34(2): 290-299.

Yoon, T.H., T.P. Trainor, P.J. Eng, J.R. Bargar and G.E. Brown Jr, Trace metal ion partitioning at polymer film-metal oxide interfaces: long-period x-ray standing wave study, *Langmuir,* 2005, Vol 21: 4503-4511.

Yokoi, H., S. Kawata and M. Iwaizumi, Interaction modes between heavy metal ions and water-soluble polymers. 2. spectroscopic and magnetic reexamination of the aqueous solutions of cupric ions and poly(acrylic acid), *Journal of the American Chemical Society,* 1986, Vol 108(12): 3361-3365.

Zhao, L., Removal of heavy metals from waste water by adsorption using chitosan membrane, Master Thesis, 2004, Department of Chemical Engineering, University of Waterloo.

APPENDICES

A1. Water sorption data and copper sulfate solution sorption data for copolymers of acrylic acid and acrylamide.

(0.500g sample in 50.00ml $CuSO_4$ solution, initial Cu^{2+}: 1300 ppm or 20.47mM)

AAc mol %	**MBA mol %**	**Water-sorption g/g**	**$CuSO_4$ solution g/g**
0	1	65.31	19.47
20	1	371.73	5.16
40	1	410.59	3.45
60	1	429.56	14.68
80	1	534.14	18.06
100	1	833.33	30.58
0	2	31.91	15.05
20	2	137.73	4.50
40	2	154.28	3.77
60	2	149.38	10.29
80	2	172.61	18.42
100	2	195.32	26.05
0	3.9	21.89	12.91
20	3.9	63.67	4.90
40	3.9	65.98	3.28
60	3.9	73.46	8.50
80	3.9	103.92	11.94
100	3.9	117.49	20.46
0	7.4	13.99	9.15
20	7.4	30.50	5.24
40	7.4	31.71	4.76
60	7.4	33.13	6.16
80	7.4	38.77	6.84
100	7.4	39.49	14.06
0	13.8	15.90	6.98
20	13.8	38.05	4.85
40	13.8	36.07	4.45
60	13.8	36.80	5.09
80	13.8	36.99	7.20
100	13.8	34.44	11.60

A2. Effect of the content of the acrylic acid on sorption uptake.

Copolymer: 75 % AAc neutralized, MBA 1 mol %

Initial Cu^{2+} concentration: 1220ppm (19.21mM)

AAc mol %	**H_2Ouptake g/g**	**$CuSO_4$uptake g/g**	**Cu^{2+} gain mmol/g**	**$CuSO_4$ bound %**	**Na^+ Loss mmol/g**
0	7.812	0.058	0.365	3.8	0.193
20	1.597	0.153	0.958	10.0	2.128
40	1.045	0.295	1.848	19.2	3.76
60	1.946	0.394	2.468	25.7	5.054
80	2.433	0.457	2.861	29.8	6.156
100	2.734	0.546	3.423	35.6	7.731

A3. Percentage of carboxyl groups neutralized by sodium hydroxide on sorption uptake.

Copolymer: 60 mol % AAc, 40 mol % AAm, MBA 1 mol%.

Initial Cu^{2+} concentration: 1550ppm (24.41mM)

Neutralized mol%	**$CuSO_4$uptake g/g**	**H_2Ouptake g/g**	**$CuSO_4$ bound %**	**Na^+ Loss mmol/g**	**Cu^{2+} Gain mmol/g**
0	0.189	0.425	9.7	0.049	1.183
25	0.302	1.444	15.5	1.717	1.889
50	0.362	1.588	18.6	3.349	2.267
75	0.396	1.644	20.3	4.226	2.482
100	0.485	1.795	24.8	5.632	3.036

A4. Effect of content of cross-linking agent on sorption uptake.

Copolymer includes AAc 60 mol % (75 % AAc neutralized), 40 mol% AAM

Initial Cu^{2+} concentration: 1220ppm (19.21mM)

MBA mol%	**$CuSO_4$uptake g/g**	**H_2Ouptake g/g**	**Cu^{2+} gain mmol/g**	**Na^+ Loss mmol/g**	**$CuSO_4$ bound %**
1	0.396	2.494	2.484	5.266	25.9
2	0.394	1.946	2.468	5.054	25.7
3.9	0.356	1.464	2.234	4.887	23.2
7.4	0.325	1.415	2.035	4.562	21.2
13.8	0.295	1.345	1.846	4.021	19.2

A5. Effect of equilibrium concentration (mM) on $CuSO_4$ and H_2O uptake

Copolymer: 60 mol % AAc (75 % AAc neutralized), 40 mol % AAm, MBA 1 mol%.

Cu^{2+} equilibrium Conc, mM	**H_2O uptake g/g**	**$CuSO_4$ uptake g/g**	**$CuSO_4$ bound %**
32.28	1.656	0.404	13.5
19.53	1.656	0.384	19.8
10.55	1.447	0.381	31.0
4.16	1.434	0.366	52.5
1.34	1.317	0.37	77.4
0.18	44.171	0.225	94.5
0.19	83.508	0.152	92.2
0.16	133.151	0.069	88.2
0.10	163.886	0.034	86.5
0.03	179.331	0.005	77.4
0	179.347	0	13.5

A6. Effect of equilibrium concentration (mM) on Cu^{2+} gain and Na^{+} loss

Copolymer: 60 mol % AAc (75 % AAc neutralized), 40 mol % AAm, MBA 1 mol%.

Cu^{2+} equilibrium Conc, mM	**Na^{+} Loss mmol/g**	**Cu^{2+} gain mmol/g**
32.28	4.245	2.533
19.53	4.269	2.403
10.55	4.247	2.39
4.16	4.377	2.291
1.34	4.533	2.315
0.18	3.02	1.408
0.19	2.155	0.952
0.16	1.249	0.435
0.10	0.796	0.215
0.03	0.455	0.033
0	0.375	0

A7. Relationship between equilibrium concentration (mM) and initial concentration

Copolymer: 60 mol % AAc (75 % AAc neutralized), 40 mol % AAm, MBA 1 mol%.

Cu^{2+} equilibrium Conc, mM	**Cu^{2+} initial Conc, mM**
32.28	37.17
19.53	24.25
10.55	15.24
4.16	8.72
1.34	5.92
0.18	3.00
0.19	2.06
0.16	0.99
0.10	0.50
0.03	0.08
0	0